MECHANICAL EVALUATION OF NANOCOMPOSITE COATINGS

Kebin Geng
University of Kentucky, eddiegeng@yahoo.com

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ABSTRACT OF DISSERTATION

Kebin Geng

The Graduate School
University of Kentucky
2006
MECHANICAL EVALUATION OF NANOCOMPOSITE COATINGS

ABSTRACT OF DISSERTATION

A dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the College of Engineering at the University of Kentucky

By
Kebin Geng

Lexington, Kentucky

Director: Dr. Eric A. Grulke, Professor of Chemical and Materials Engineering

Lexington, Kentucky

2006

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An anti-reflective (AR) lens is an ultrathin multilayered structure composing of AR coatings on a lens substrate. These coatings can be made by a spin-coating process with a nanocomposite of UV curable acrylic monomers and well dispersed metal oxide nanoparticles. The in-situ UV polymerization rate was reduced by oxygen inhibition and the absorption of UV energy by the metal oxide nanoparticles.

There are few studies of the mechanical properties of ultrathin polymeric coatings that include the effects of substrates, the viscoelastic behaviors of polymers in submicron scales and the effects of multilayered coatings. With a coating system based on UV cured dipentaerythritol pentaacrylate on silicon wafer substrates, nanoindentation tests showed that the nominal reduced contact modulus increased with the indentation load and penetration depth due to the effect of the substrate, in quantitative agreement with an elastic contact model. Ultrathin polymeric coatings subjected to constant indentation loads exhibit shear-thinning during flow.

None of the models examined completely described the elastic response of an ultrathin polymeric coating on a compliant plastic substrate. The effective modulus was a function of coating-substrate property, indenter tip size, coating thickness, adhesion and residual stress. It was logarithmic dependent on the ratio of the indentation depth to the coating thickness prior to coating fracture.
An elastic model, assuming shear-lag and a plane-stress state, was used to estimate the interfacial strength between a submicron coating and a compliant substrate. The critical indentation load for the indentation-induced delamination of the coating from the substrate increased with the third power of the indentation depth and was a linear function of the reciprocal of the coating thickness. The interfacial strength was 70.4 MPa.

Mechanical properties and fracture characteristics of CVD ceramic and nanocomposite coatings on polymer substrates were evaluated by nanoindentation and nanoscratching tests. The AR lenses made with polymer nanocomposite coatings have better mechanical properties due to the close match of properties between the coatings and the plastic substrate. The new approach to making AR lenses with polymer nanocomposites on plastic substrate is promising.

KEYWORDS: Polymeric coating; Nanoindentation; modulus; interfacial strength; nanocomposite
MECHANICAL EVALUATION OF NANOCOMPOSITE COATINGS

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By
Kebin Geng
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Chapter One: Introduction

1.1 General description of the dissertation

Nanocomposites have been attracting great attention from purely academic research, extending to commercialization in recent years. Formulation and processing of polymer nanocomposite coatings, composed of inorganic nanoscale fillers and UV curable monomers, are a major active research area of nanocomposites. The aim of these activities is to maximize the unexpected extraordinary properties of nanocomposites to fabricate various layered structures and devices in micron-scales and nanoscales. However, there are many fundamental physicochemical phenomena that need to be understood, and fabrication and characterization methods applied for nanocomposite coatings need to be well established.

An anti-reflective (AR) lens is a typical layered structure composed of multilayered AR coatings and often a scratch-resistant coating with the thickness varying from 50 nm to 3 μm on a lens substrate, usually a plastic plate nowadays. An AR lens is traditionally made by chemical vacuum deposition methods. This is the main industrial method to develop multilayered ceramic coatings on lenses. While utilizing a plastic as the lens substrate, the mismatch in mechanical behavior between the ceramic coating and the plastic substrate has caused problems. Surface damage, including scratches and cracks, induces haze on the AR coatings, reducing the transmission of the optical article. A new approach of fabricating AR lenses by an in-mold spin coating method, with the antireflective coatings incorporating ¼ wavelength thin films based on a polymer nanocomposite, is compared with the traditional ceramic AR lenses by mechanical evaluation in detail, namely, nanoindentation and nanoscratching tests.

The new approach described in this dissertation to fabricate nanocomposite coatings is a process of dispersing nanoscale inorganic composites in an acrylic monomer system and then conducting an in-situ UV polymerization. There are many factors that could affect the UV polymerization process. Oxygen inhibition could retard the UV polymerization kinetics and C=C double bond conversion rate if the polymerization occurs in the presence of oxygen. Different metal oxide fillers could
absorb UV light differently at a broad wavelength, and thus the polymerization rate and the polymerization degree across the thickness of a coating could vary. Thickness of coating could also be a factor for UV polymerization process. To understand these reaction factors could lead to optimal polymerization conditions at which the cured material has balanced mechanical and adhesion properties. Traditional chemical analytical methods such as FTIR may not be adequate for providing this information. A new approach to monitoring the process using nanoindentation and nanoscratching tests will be presented.

The measurement of mechanical properties near polymer surfaces is helpful to provide improved understanding of the unique behavior of polymers near the surface and improved control of the fabrication and polymerization processes of multilayer materials. However, there are few studies of the mechanical properties of ultrathin polymeric films that include the effects of substrates, viscoelastic behaviors of polymers in submicron scales and the effects of multilayered films. Unlike the thicker coatings that can be measured by conventional methods, such as a tensile test, nanoindentation has proved to be a powerful tool to measure directly the mechanical properties of submicron polymeric coatings.

Many models for compliant coatings on stiff substrates have been reported. However, there is no generally accepted model for the case of a stiff coating on a compliant substrate. Models to separate the elastic modulus of the stiff coating from the compliant substrate are only applicable for specific coating-substrate systems.

Surface damage and interfacial failure may affect the performance of coating systems and limit the reliability of devices. Thus, reliable characterization of interfacial strength is critical to the improvement of adhesive properties and to the control of quality in multilayer structures and devices. The traditional peel test, buckling test and blister test are not quantitative or requiring complicated sample preparation and they are difficult for evaluating ultrathin coatings. Accurate and rapid methods for submicron coatings would be particularly useful for product development, design, and quality control applications.
This dissertation work was funded by Optical Dynamics Corporation with the aim to establish a precise and repeatable method to mechanically evaluate ultrathin polymeric nanocomposite coatings on lens substrates.

1.2 Scope of this dissertation

This dissertation is composed of eight chapters in the following order: fabrication of nanocomposite AR coatings (Chapter Two), nanoindentation and nanoscratching techniques (Chapter Three), mechanical evaluation of ultrathin coatings on both the stiff substrate (Chapter Four) and the compliant substrate (Chapter Five) as well as delamination (Chapter Six) and fracture phenomena (Chapter Seven), and important future work (Chapter Eight).

The general materials and fabrication methods of anti-reflective (AR) lenses, as an example of multilayered nanocomposite coatings, will be introduced in Chapter Two. The inherent problems associated with the traditional vacuum deposition method, when forming the ceramic AR coatings on plastic substrates, will be pointed out and then a new approach of an in-mold spin-coating process using polymer nanocomposites will be presented as a potential alternative method. The nanocomposite coatings to be discussed are formulated with well-dispersed metal oxide nanoparticles in UV curable acrylic monomers. Factors, such as oxygen inhibition, transitional metal oxide nanoparticles and the thickness of the coatings, will be studied to determine their influence on the polymerization kinetics and the maximum C=C double bond conversion rate. A brief literature survey will be presented about the unique properties of polymers near the surface, which could be a factor to affect the fabrication of submicron AR polymer nanocomposite coatings. The typical characterization methods that are needed for fabricating the nanocomposite AR lenses will be listed in the end of the Chapter.

A direct measurement of the mechanical properties of the ultrathin AR coatings is critical for fabricating the AR lenses. Nanoindentation and nanoscratching testing techniques as the most popular and powerful tools for this purpose are introduced in Chapter Three. The classic Oliver & Pharr’s equation is a widely accepted model for calculating the elastic modulus of a half-space material, but is not applicable for a thin coating-substrate system due to the substrate effect and the inaccurate estimation of
the indentation contact area. A literature survey is conducted for the effective elastic response of a coating-substrate system. Since the substrate deformation is more significant and appears at the very smaller indentation load when a compliant substrate instead of a stiff substrate is used, a series of empirical and analytical models, which could be potentially applicable for a stiff coating on a compliant substrate, are presented. The principles of nanoscratch testing are introduced because nanoscratching testing is a good way to evaluate the adhesion between each AR coatings and these coatings to a substrate, and the fracture toughness. The calibrations of the instrument in both nanoindentation and nanoscratching testing modes are described and the detailed step by step procedures are attached in Appendix B.

In Chapter Four, a series of model polymer coatings with thickness of 47 nm, 125 nm and 3000 nm are spin-coated and UV cured on silicon wafer substrates. Nanoindentation is applied to study the effect from the stiff substrate and the viscoelastic deformation of these ultrathin polymeric coatings. A model addressing the stiff substrate effect with a more accurate indentation contact area function is derived. The reduced elastic moduli from the experiment data are re-calculated and compared with the results from the classic Oliver & Pharr’s model which has been integrated in the instrument as a default calculation method.

Chapter Five will study the elastic response of the same polymer coatings used as in Chapter Four on the compliant plastic substrates. Four potentially successful empirical and analytical models are examined to determine the validity for this polymeric coating on a plastic substrate system. Although none of the models may be completely applicable for a wide range of the indentation penetration depths, the study helps to show key factors that need to be considered for the modeling: the ratio of elastic modulus between the coating and the substrate, the indenter tip size, the coating thickness, the adhesion property between the coatings and the substrates, and the residual stress existing in the coating and at the interface. A logarithmic relation is found between the effective modulus and the ratio of the indentation depth to the coating thickness. This relation could be very important for generating a modeling applicable to an ultrathin polymer coating on a compliant substrate in the future.
Adhesion of a coating to a compliant substrate is discussed in Chapter Six. The study is conducted by evaluating the coating thickness effect on the critical indentation load that initiates the delamination between the coating and the substrate under a nanoindentation impression stress. An elastic model will be developed to estimate the interfacial strength between a submicron surface coating and a compliant substrate. The analysis uses a shear-lag model and assumes the plane-stress state in the surface coating. The validity of this assumption will be verified for submicron coatings as well as for the micron coating in the experiment. The interfacial strength will be estimated using the model developed.

The overall mechanical properties of AR lenses made with ceramic coatings by chemical vacuum deposition and AR lenses made with polymer nanocomposite coatings by an in mold spin-coating process are evaluated by nanoindentation and nanoscratching tests in Chapter Seven. The effective elastic moduli at a wide indentation depth of the multilayered coatings are measured and compared using a nanoindentation method. Combined with the AFM and SEM images of the resulting indentations and scratches imprints, including the fracture phenomena of the two types of material coatings on plastic lens substrates, are presented. These results are sufficient for evaluating the AR lenses made by the two different approaches.

In Chapter Eight, a model for the kinetics of UV polymerization is proposed for the future work in order to optimize the formulation and curing conditions when fabricating submicron polymeric nanocomposite coatings. Some preliminary data are presented. A general conclusion of this dissertation will be given in Chapter Nine.
Chapter Two: An example nanocomposite – multilayered optical lenses

In this chapter, general principles and procedures are introduced on how to formulate and fabricate AR coatings for AR lenses. First of all, a brief survey will be given on nanocomposite materials and nanocomposite coatings. Then, as an example of multilayered nanocomposite coatings, AR coatings are introduced and the reason is pointed out why to fabricate nanocomposite AR coatings instead of traditional ceramic AR coatings. The raw materials and the fabrication method for nanocomposite coatings are given. The UV polymerization process and its influencing factors are discussed. A brief literature survey will be presented about the unique properties of polymers near the surface, which could be a factor to affect the fabrication of submicron AR polymer nanocomposite coatings. The typical characterization methods that are needed for fabricating the nanocomposite AR lenses will be listed in the end of the Chapter.

2.1 Nanocomposites

The nanocomposite concept was introduced as early as 1970 (Theng 1970). It is generally defined as a material composed of two or more distinctively dissimilar components existing at different phases. Among them, at least one component has a nanometer scale in one dimension (length, width or thickness). The continuous phase, or matrix, can be various materials, such as ceramic (Liu, Chen et al. 2003; Neralla, Kumar et al. 2004), metal (Scanlon and Cammarata 1994; Oberle, Scanlon et al. 1995) or polymeric (Penumadu, Dutta et al. 2003; Pomogailo 2005; Pomogailo 2005; Lach, Kim et al. 2006). A polymer nanocomposite usually consists of a nanoscale inorganic component in various shapes (particles, tubes or discs) dispersed in an organic polymer matrix (Penumadu, Dutta et al. 2003; Pomogailo 2005; Pomogailo 2005; Lach, Kim et al. 2006). These inorganic-organic hybrids sometimes are named as “Ceramers” by Wilkes (Wilkes, Orler et al. 1985; Tamami, Betrabet et al. 1993; Jordens and Wilkes 2000; Jordens and Wilkes 2001; Wilkes and Li 2003) and named as “ORMOSILs”, especially when using silica particles by Schmidt (Lintner, Arfsten et al. 1988; Schmidt and Popall...
In this dissertation, “nanocomposites” will always refer to polymer-based nanocomposites compositing of various metal oxide nanoparticles.

Nanocomposites have been attracting great attention in recent years because of their unexpected extraordinary properties, resulting from synergism between the properties of the parent components and from the interfacial interactions (Pomogailo, Rosenberg et al. 2003; Pomogailo 2005; Lach, Kim et al. 2006; Yang 2006). Compared to conventional hybrid composites (both micro and macrocomposites), nanocomposites have some unique properties, such as mechanical properties (greatly increasing stiffness without sacrificing the impact strength (Usuki, Kawasumi et al. 1993; Cox, Dear et al. 2004), thermal stability (Lan, Kaviratna et al. 1994), flame retardant properties (Lan, Qian et al. 2002), barrier properties (Kojima, Fukumori et al. 1993; Kojima, Usuki et al. 1993; Gilmer, Barbee et al. 2002), optical properties, rheological properties, ease of biodegradation (Hiroi, Ray et al. 2004; Okamoto 2004; Okamoto 2006), chemical resistance and others (Haas, Amberg-Schwab et al. 1999; Kickelbick 2002; Rose, Posset et al. 2002). The exceptional properties of polymer nanocomposites are related to three mechanisms: (1) polymer chains are confined by the nanoscale particles, which are in the size range (5-20 nm) of the radius of gyration of the polymer chains, (2) the nanoscale inorganic particles themselves have unique mechanical, optical and electrical properties that are superior to macroscopic particles, and (3) the way these nanoscale constituents are arranged (Glasel, Hartmann et al. 1999). In addition, the exceptional properties are also contributed by the interfacial interaction at the extremely large contact interfaces of the nanoparticles and the polymer matrix; this interaction dissipates huge energy during a deformation (Nelson, Utracki et al. 2004; Pucciariello, Villani et al. 2004; Suhr, Koratkar et al. 2006).

The nanocomposites' unique properties have helped not only to improve existing products, but also to extend their applications into the areas formerly dominated by metal, glass and wood in the appliance, construction, electrical, food packaging and transportation industries (LeBaron, Wang et al. 1999; Ray and Okamoto 2003; Okamoto 2004; Paquette, Dion et al. 2006; Paquette, Dion et al. 2006). However, only the polymer/inorganic particle type of polymer nanocomposites has been realized for significant commercial applications (Lan, Kaviratna et al. 1994; Bagrodia, Gilmer et al. 2005).
For example, a 2% layered silicated nanoparticle reinforced polyolefin can increase the heat distortion temperature (HDT) by up to 100°C, which make it feasible to mold the composite for under-the-hood parts in automobiles (Usuki, Kawasumi et al. 1993; Cox, Dear et al. 2004).

The nanocomposite coatings are another major commercial application. They have been applied as scratch resistant painting for automobiles (Cox, Dear et al. 2004) (Schneider, Ragan et al. 2002), anti-corrosion coatings for metals (Zhang, Wang et al. 2002; Shah 2004; Yu, Yeh et al. 2004; Asmatulu, Claus et al. 2005; Lyn, Park et al. 2005), flame retardant reinforced materials (Tong 2002; Ebrahimian, Jozokos et al. 2004; Okoshi and Nishizawa 2004; Prigent and Vanpouille 2005; Qin, Zhang et al. 2005; Wang, Han et al. 2006), shape memory materials (Gall, Dunn et al. 2002), medical implant materials such as dental materials (Wei, Jin et al. 1998), and optical filters in optoelectronic systems (Mennig, Oliveira et al. 1999; Zhou, Xiong et al. 2003) (Bi, Kumar et al. 2001; Kambe, Blum et al. 2002; Kambe and Honeker 2003; Bauer and Mehnert 2005).

An anti-reflective (AR) lens is typically a layered structure composed of multilayered AR coatings and often a scratch-resistant coating with a thickness between 50 nm and 3 μm on a lens substrate, which is popularly a plastic plate in this decade (a glass plate in old years). An AR lens is traditionally made by a chemical vacuum deposition method to deposit the multilayered ceramic coatings on a lens substrate. It is found that, while utilizing a plastic as the lens substrate, the mismatch in mechanical behavior between the ceramic coatings and the plastic substrate has caused problems. This dissertation introduces a new approach of fabricating AR lenses by an in-mold spin-coating method, with the antireflective coatings made from polymer nanocomposites. These nanocomposite coatings are fabricated by the process of dispersing nanoscale inorganic composites in an acrylic monomer system, spin-coating on a substrate and then conducting an in-situ UV polymerization.

UV polymerization is greatly affected by monomer chemistry, photoinitiator type, oxygen inhibition, metal oxide nanoparticles and coating thickness. An UV polymerization process needs to be understood fundamentally in order to achieve fast reactions, controllable monomer conversions, uniformity across the coating, optimal
mechanical properties and to eliminate the spin-coating defects for the ODC’s AR lens fabrication, since the polymerization degree and uniformity determine the mechanical properties and the adhesion strength between the coating and the substrate. Traditional chemical analytical methods such as FTIR may not be adequate for providing this information. A novel approach to monitoring the process using nanoindentation and nanoscratching tests will be presented. It has been proved that they are powerful tools to measure directly the mechanical properties of these ultrathin multilayered nanocomposite coatings. The work of this dissertation, mainly applying nanoindentation and nanoscratching techniques to directly measure the mechanical properties of as-produced multilayer nanocomposite coatings, has greatly accelerated ODC’s coating development, materials selection and structural design processes.

2.2 Nanocomposite coatings for AR lenses

2.2.1 Introduction of AR lenses

Thin-film optical filters have been around for over a century and chemical vapor deposition techniques have predominately been the manufacturing choice, particularly when glass is used as the lens material. The technique generally includes the deposition of metal-oxide ¼ wavelength thin-film layers of varying refractive index to change the optical efficiency of the surface of a substrate. These can include broadband antireflective and reflective coatings as well as edge- and band-gap filters (Macleod 2001). Antireflection coatings over the visible spectrum (380 nm to 780 nm) are the predominant use for these filters with uses in ophthalmic lenses, solar cells, data storage and other optical devices requiring high optical transmission. The reflectance spectrum of an ophthalmic lens is shown in Figure 2.1. The uncoated lenses typically have about 4% reflectance in general (the blue line is not measured) and the AR coatings can reduce the reflectance by about 70% at the wavelength range of 530 – 630 nm, which is the radiation to which human eyes are most sensitive, as shown in Figure 2.2.
Figure 2-1 An example of reflectance spectrum of lens surface over visible region with and without AR coatings (Courtesy of ODC)
Figure 2-2 The relative human eye sensitivity in the visible light range

2.2.2 A new approach to make an AR lens on a plastic substrate

Traditional vacuum deposited anti-reflective coatings have been around since the 1930’s and actually perform well when coated on a glass ophthalmic lens since the coatings themselves are ceramic. In this layering system, both components have similar thermal expansion coefficients, similar mechanical properties, and good interfacial adhesion. During the 1970’s, manufacturing improvements allowed polymer lenses to gain general acceptance as an alternative for glass; however, traditional anti-reflective coatings did not fare well on plastic substrates due to the major differences in the strain behavior of the coating and the lens. Significant progress has been made in this technology, but the disparity in the strain domains continues to be an issue.

Spin-on glass coatings via the sol-gel process and hybrid materials have also been proposed, but these have not gained acceptance in the marketplace. Optical Dynamics Corporation was the first company to commercialize the new approach by using polymer nanocomposites in the United States. An AR lens is typically composed of two types of coatings on a plastic lens substrate: multilayered AR coatings with different refractive index at each layer and a scratch-resistant coating. The each layer of AR coatings has a thickness on the order of 50~100 nm and the scratch resistant coating is about 3 μm. The thickness of the AR coatings is critical for desired AR performance and the tolerance of the thickness needs to be controlled within about ±5 nm. The structure of a simple AR filter is shown in figure 2.3, and more complicated stacks can be used to improve the optical efficiency. The nanocomposite materials are formulated with well dispersed metal oxide nanoparticles into UV / thermal curable acrylic monomers.

The goal of this project was to fabricate the AR lens with polymer nanocomposites and to compare the mechanical performance with the traditional vacuum deposition techniques.
Figure 2-3  A schematic structure of an AR lens made with polymer nanocomposites  
(Courtesy of ODC)
2.3 Fabrication of nanocomposite ultrathin coatings

There are numerous methods to fabricate nanocomposites with continuous organic domain which could be categorized into three approaches. The first route is to disperse nanoscale inorganic composites into a polymer matrix (Takahashi, Kakimoto et al. 2005). The second route is to form a nanocomposite by dispersing nanoscale inorganic composites in a monomer system and then perform in-situ polymerization (Kojima, Usuki et al. 1993; Xu, Li et al. 2003; Druffel, Geng et al. 2006). A third route is to condense the solid inorganic phase in-situ of polymer matrix Okamoto 2006(Ballard, Williams et al. 2000; Kickelbick 2002; Schubert, Husing et al. 2002), which is usually chosen for the optimal dispersion of nanoscale particles in the polymer matrix. In this study, the nanocomposite coatings are fabricated in the second route as described above.

2.3.1 Materials

2.3.1.1 Metal oxide nanoparticles

Metal oxide nanoparticles were selected for two general purposes: mechanical reinforcement and refractive index properties (Kambe, Kumar et al. 2002; Krogman, Druffel et al. 2005). Table 2.1 presents a number of types of metal oxide nanoparticles potentially applicable for AR coatings. Titania, ceria, zirconia and Ta$_2$O$_5$ are good for formulating high reflective layers, silica is good for low index layer; alumina and silica have excellent mechanical properties and are preferred for fabricating the scratch-resistant coating (Kambe, Kumar et al. 2002) (Krug, Tiefensee et al. 1992; Chisholm 2005).
Table 2-1  Metal oxide nanoparticles for the nanocomposite AR lenses

(CRC Handbook and Angus Macleod)

<table>
<thead>
<tr>
<th>Material</th>
<th>Mohs Hardness</th>
<th>Refractive index at 550-600 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al₂O₃</td>
<td>9</td>
<td>1.62</td>
</tr>
<tr>
<td>SiO₂</td>
<td>7</td>
<td>1.46</td>
</tr>
<tr>
<td>TiO₂</td>
<td>6</td>
<td>2.2-2.7</td>
</tr>
<tr>
<td>ZrO₂</td>
<td>6.5</td>
<td>2.10</td>
</tr>
<tr>
<td>ZnO</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>CeO₂</td>
<td>6</td>
<td>2.20</td>
</tr>
<tr>
<td>Ta₂O₅</td>
<td></td>
<td>2.16</td>
</tr>
<tr>
<td>Polymer</td>
<td></td>
<td>1.48</td>
</tr>
</tbody>
</table>
In order to be used in an optical coating, the particle size and dispersion are very critical. Usually only the metal oxide nanoparticles with the size of less than 40 nm are selected for high transparency. There are a number of metal oxide nanoparticles commercially available. It is important to study the dispersion and stability of these metal-oxide nanoparticles in the monomers.

There are a number of methods for dispersing nanoparticles, all of which are based on using various forms of energy (Mandzy, Grulke et al. 2005; Yang, Grulke et al. 2005). These include: mixing with conventional agitators, colloid mills (Pohl and Schubert 2003), ultrasonication (Olivi-Tran, Botet et al. 1998) (Pohl and Schubert 2003) and bead mills (Gajovic, Stubicar et al. 2001; Stefanic, Music et al. 2006). There are two methods for stabilizing dispersions: (1) electrostatic stabilization (Mandzy, Grulke et al. 2005), (2) steric stabilization (short chain coupling agents or long chain coupling agents) (Scherer 1990). By adding acidic or alkaline reagents in aqueous system, a pair of double electrical layers (ions and counterions) forms around the particle to create repulsive forces to overcome the attractions leading to agglomeration. The adsorbed layer of organic molecules on the surface of particles discourages agglomeration by entropic and enthalpic mechanisms (Scherer 1990).

2.3.1.2 Monomers

There are various UV curable acrylic monomers commercially available. Table 2.2 lists some of the monomers supplied by Sartomer. Monomers containing carbon-carbon double bonds can be cured using photoinitiators and UV light. The Sartomer family of monomers has between one to five carbon-carbon double bonds per molecule, different chain lengths between reactive units, and different constituents along the chain segments. Monomers with one C=C bond will polymerize to linear molecules, while those with more than one carbon-carbon bonds per molecule will give crosslinked chains. The higher the number of double bonds per monomer gives higher degrees of cross-linking, and more rigid polymers. Monomers with lower functionality usually have lower viscosity which is good for coating processing. The more ethoxy groups in a molecule, the more hydrophilic the monomer will be. Hydrophilic polymers can help the dispersion of metal oxide nanoparticles in alcohols, ketones, and water.
In order to improve the coating mechanical properties and the adhesion strength to a substrate, there are some commercial available acrylic derivatives, such as acrylated epoxy, acrylated urethane, acrylated polyether and acrylated polyester monomers or oligomers (Hoyle 1990).

The overall mechanical properties are controlled by the functionality, molecular weight, number of the chemical structures per repeating unit, and curing conditions. The mechanical properties can be evaluated from the manufacturer’s specification and also can be directly measured by a nanoindentation technique. The measured elastic modulus and hardness data were also shown in Table 2.2.

A representative high functionality acrylic monomer, dipentaerythritol pentaacrylate, is commercially available from Sartomer (SR399, CAS# 60506-81-2). After polymerization, it forms a densely cross-linked polymer exhibiting good mechanical strength, thermal stability and resistance to solvent absorption which is ideally suited as surface protective coatings and dental restorative materials (Anseth 1996). SR399 was chosen as a model monomer for this dissertation study. The molecular structure of the SR399 monomer is shown in Figure 2.4.
### Table 2-2 Some of the UV curable acrylic monomers from Sartomer

<table>
<thead>
<tr>
<th>Monomer</th>
<th>Modulus* Gpa</th>
<th>Hardness* Gpa</th>
<th>molecular weight g/mol</th>
<th>Functionality</th>
<th>Ethoxyl-ation #</th>
<th>Tg, 0C manuf. spec.</th>
<th>Refrac- tive index</th>
<th>Chemical name</th>
<th>Chemical structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>SR399</td>
<td>4.04</td>
<td>0.46</td>
<td>525</td>
<td>5</td>
<td>0</td>
<td>90</td>
<td>1.49</td>
<td>dipentaerythritol pentaacrylate</td>
<td><img src="image1" alt="Chemical structure" /></td>
</tr>
<tr>
<td>SR351</td>
<td>3.64</td>
<td>0.332</td>
<td>296</td>
<td>3</td>
<td>0</td>
<td>62</td>
<td>1.47</td>
<td>trimethylopropane triacrylate</td>
<td><img src="image2" alt="Chemical structure" /></td>
</tr>
<tr>
<td>SR454</td>
<td>2.48</td>
<td>0.08</td>
<td>428</td>
<td>3</td>
<td>3</td>
<td>1.47</td>
<td>ethoxylated(3) trimethylpropane triacrylate</td>
<td><img src="image3" alt="Chemical structure" /></td>
<td></td>
</tr>
<tr>
<td>SR499</td>
<td>1.00</td>
<td>0.08</td>
<td>560</td>
<td>3</td>
<td>6</td>
<td>-8</td>
<td>1.47</td>
<td>ethoxylated(6) trimethylpropane triacrylate</td>
<td><img src="image4" alt="Chemical structure" /></td>
</tr>
<tr>
<td>SR238</td>
<td>1.05</td>
<td>0.088</td>
<td>226</td>
<td>2</td>
<td>0</td>
<td>43</td>
<td>1.46</td>
<td>1,6 hexanediol diacrylate</td>
<td><img src="image5" alt="Chemical structure" /></td>
</tr>
<tr>
<td>SR344</td>
<td>1.01</td>
<td>0.04</td>
<td>508</td>
<td>2</td>
<td>n</td>
<td>3</td>
<td>1.47</td>
<td>polyethylene glycol (400) diacrylate</td>
<td><img src="image6" alt="Chemical structure" /></td>
</tr>
</tbody>
</table>

* Measured by nanoindentation after UV cured at 4 mW/cm² for 90 sec in presence of CO₂
Figure 2-4  Molecular structure of SR399 monomer
2.3.1.3 Photoinitiator

Acrylic monomers are usually free radical polymerized. The free radical reaction is initiated by dissociation of the photoinitiator molecules under UV radiation. The type of photoinitiator is often chosen having a relative high extinction coefficient in the region of the electromagnetic spectrum matching the output of the lamp source used. Besides, it is capable of producing free radicals efficiently with high yield, and the generated free radicals are capable of rapidly initiating polymerizations (Hoyle, photocurable coating). A representative free-radical photoinitiator, 1-hydroxy cyclohexyl phenyl ketone (Irgacure 184, purchased from Ciba-Geigy, CAS# 947-19-3), is shown in Figure 2.5. This photoinitiator absorbs UV light significantly and decomposes efficiently at the wavelength of 256 cm\(^{-1}\) (see Figure 2-8). Irgacure 184 is typically added at about 5% weight with respect to monomers that are previously dissolved in equal weights of acetone and isopropanol co-solvents. A germicidal lamp is used as the UV source that its strongest UV light emission is at the wavelength of 256 cm\(^{-1}\).
Figure 2-5  Photoinitiator: 1-hydroxy cyclohexyl phenyl ketone (Ciba-Geigy Irgacure 184)
2.3.2 UV polymerization process

2.3.2.1 Curing conditions

The ultrathin nanocomposite AR coatings were fabricated in a multiple-step process in the order of dispersing metal oxide nanoparticles in an acrylic monomer system usually containing solvents (alcohols and/or ketones), spin-coating on a flat substrate (for example, a stiff silicon wafer or a compliant plastic plate) and then conducting an in-situ UV polymerization. The thickness and surface quality of the ultrathin polymeric thin coatings were controlled by the solute concentration and spin speed (Meyerhofer 1978). A germicidal lamp was used for the UV polymerization modeling study and has an intensity of 4mW/cm\(^2\) at 5 cm distance. The UV polymerization was conducted at the ambient temperature and in the presence of CO\(_2\), except when stated in the presence of air.

A typical recipe for a model UV polymerization study consists of 5 weight percent of the photoinitiator Irgacure 184 dissolved in the penta-functional acrylic monomer SR399, which is then dissolved in a solution of equal weights of acetone and isopropanol co-solvents.

The polymerization degree or [C=C] conversion rate was monitored by FTIR. There is a characteristic infrared absorption peak of 809 cm\(^{-1}\) for an acrylic monomer (CH=CH\(_2\) twisting). The amount of the absorption at this peak can be used quantitatively to calculate the polymerization degree (Decker and Jenkins 1985; Decker and Moussa 1989). For the kinetics study, these ultrathin coatings were spin-coated on KBr plates directly and the residual [C=C] concentration was monitored by FTIR using a transmission testing mode.

2.3.2.2 Factors affecting UV photopolymerization

Photopolymerization of acrylic polymers have been extensively studied (Fouassier 1995) (Decker and Jenkins 1985; Anseth 1996; Mehnert, Hartmann et al. 2001; Studer, Decker et al. 2003). UV curable monomers are usually multifunctional and can be cured under UV or electron beam radiations very quickly (Anseth 1996). There are some factors that affect the kinetics of the polymerization process, such as type of
photoinitiator, UV type and intensity, oxygen effect (Decker and Jenkins 1985; Studer, Decker et al. 2003; Lee, Guymon et al. 2004), coating thickness (Decker and Moussa 1989; Medvedevskikh, Zagladko et al. 2000), filler effect (Cho, Ju et al. 2005) and reaction medium (Lalevee, Allonas et al. 2006).

A model nanocomposite system of CeO\(_2\)/SR399/Irgacure184 (weight ratio: (0-80)/100/5) coatings was studied for kinetics of an UV polymerization. The coatings were spin-coated on KBr plates and cured under an UV radiation of intensity of 40 W/m\(^2\) in the presence of air and inert CO\(_2\). The absorption amounts at the peak of 809 cm\(^{-1}\) were measured to calculate the [C=C] conversion rate. The results are shown in Figure 2.6 and Figure 2.7.

The photoinitiator, the oxygen inhibition and the filler effects have been experimentally detected from the model UV polymerization system study as shown in Figure 2.6. For comparison, the thickness of all the coatings was controlled at 220 nm, measured by a profilometer. The observations are: (1) after UV radiation of 30 seconds at the same curing conditions in CO\(_2\), the [C=C] conversion rate was 82% when using photoinitiator Irgacure 184, while only 17% without photoinitiator. (2) In the inert carbon dioxide environment, the polymerization was very quickly and the conversion of C=C reached 82% within five seconds. However, the polymerization apparently slowed down at the induction period and the maximum conversion rate was about 20% less in the presence of air comparing with the curing in CO\(_2\). And (3) the ceria metal oxide nanoparticles significantly retarded the polymerization process and reduced the maximum [C=C] conversion rate to 57% after 30 sec radiation in contrast to 82% for a coating with no fillers at the same curing conditions.

Therefore, the photoinitiator is essential for an UV polymerization by quickly providing free radicals to initiate the curing reaction. In the presence of air, oxygen molecules diffusing from the gas phase into a coating can quench the initiator and scavenge both initiating and the polymer radicals by forming much less active peroxyl radicals, resulting in a slower polymerization rate and a lower [C=C] conversion (Decker and Jenkins 1985; Decker and Moussa 1989; Khudyakov, Legg et al. 1999). Since the oxygen molecules diffuse faster in a thinner coating than in a thicker coating, the oxygen effect is expected to have more influence for a thinner coating than for a thicker
coating during a curing process. This phenomenon was observed for a model coating system in Figure 2.7. These coatings were SR399/Irgacure184 at the thickness of 47 nm, 125 nm and 3000 nm which were spin-coated on KBr plates respectively and cured with the germicidal lamp in air. The [C=C] conversions were 58%, 66% and 82% for 47 nm, 125 nm and 3000 nm coatings respectively under UV radiation for 30 seconds. The data demonstrated the strong thickness effect of the SR399 coatings in the presence of the oxygen, as reported in literature (Decker and Moussa 1989; Decker 1992).

The extinction coefficient $\varepsilon$, a measure of the amount of light absorbed per unit concentration, was calculated from the UV absorption of the material based on the Beer-Lambert as in the form (Decker 1992),

$$A = \varepsilon b c$$  \hspace{0.5cm} 2.1

$$A = -\log\left(\frac{I}{I_0}\right)$$  \hspace{0.5cm} 2.2

In which, $A$ is the light absorption, $b$ is the path-length of an UV light, $c$ is the mole concentration of a material, $I$ is transmitted light intensity and $I_0$ is the incident light intensity.

In this work, the UV absorption was measured by a Hewlett Packard model 8453 spectrophotometer. Samples can be dissolved or suspended in ethanol or other low UV absorption solvents and contained in a fused silica cuvette with an optical path-length of 1 cm. The absorption of a sample was obtained after the subtraction of the background absorption by the solvent used. Therefore, only water and alcohols but not ketones were used.

The calculated extinction coefficients of Irgacure 184, TiO$_2$ CeO$_2$, SiO$_2$ and SR399 were obtained as 11400, 8440, 3600, 990 and 1 $\left(\text{liter} \left(\text{cm} \times \text{mole}\right)\right)$, respectively, at the wavelength of 256 nm where the most strong emission of UV lights is by a germicidal lamp, shown in Figure 2.8. All nanoparticles were in the order of 10-30 nm in size, measured by a particle size analyzer or by TEM. Obviously, the photoinitiator Irgacure 184 has a very high extinction coefficient and the acrylic monomer has a negligible one. The majority of UV intensity will be absorbed by the photoinitiator for dissociation in a SR399/Irgacure184 coating system, which results in a very rapid
polymerization. However, if the coating is composed of transitional metal oxide nanoparticles, such as TiO$_2$ or CeO$_2$, a significant interference on the UV polymerization, due to the filler’s strong light absorption at 256nm, is expected, likely producing a gradient polymerization degree across the coating thickness. In this case, Irgacure 184 is not an ideal photoinitiator. It is noticed that the absorption of TiO$_2$ and CeO$_2$ decreases greatly at a wavelength of over 300 nm. A photoinitiator that can be dissociated efficiently at a wavelength of over 300 nm is preferred in order to overcome this “pigment screen effect” (Hoyle 1990).

The extremely low extinction coefficient of SiO$_2$ nanoparticles at a broad of UV range (200-500 nm) and the good mechanical properties of SiO$_2$ make it a primary choice for fabricating thicker protective coatings (Bauer, Ernst et al. 2000; Zhang, Wang et al. 2002; Xu, Li et al. 2003; Zhou, Xiong et al. 2003; Cho, Ju et al. 2005; Lach, Kim et al. 2006). Interestingly, it is reported that silica nanoparticles could accelerate an UV polymerization of an acrylic monomer system, probably due to the synergistic effect of silica nanoparticles during the photopolymerization (Cho, Ju et al. 2005).

It is worth pointing out that, unlike a low functional acrylic monomer, a high functional acrylic monomer has higher reactivity but a higher viscosity and a lower gelation point during the curing. The high viscosity hinders the segmental mobility (T$_g$ below ambient) of the polymer free radicals and the residual monomers. Therefore, although a high functional acrylic monomer polymerizes faster, the maximum attainable [C=C] conversion is lower than that of a lower functional acrylate (Decker and Moussa 1989) (Anseth 1996; Khudyakov, Legg et al. 1999; Khudyakov, Purvis et al. 2003).

Since the UV polymerization is a complicated reaction and influenced by so many factors, a through research is necessary. Therefore, some preliminary kinetic study of UV polymerization will be reported in Chapter Eight.
Figure 2-6  The effects of oxygen inhibition, photoinitiator and filler absorption on an UV polymerization
Figure 2-7  Thickness effect on an UV polymerization in the presence of the oxygen
Figure 2-8  The extinction coefficients of TiO$_2$ and CeO$_2$ nanoparticles, photoinitiator 184 and polymer SR399
2.3.3 Spin-coating process for ophthalmic lenses

The substrate used is an acrylic flat made by Optical Dynamics Corporation. The ophthalmic lenses are made using the in-mold casting technology (nanocomposite) which yields an anti-reflective thin film approximately 300 nm thick. The spin-coating processes are described in the following paragraphs.

The anti-reflective layers are first applied to the molds in reverse order as the coatings in a finished AR lens, using a spin coater by Optical Dynamics Corporation. The air within the coater is HEPA filtered to keep defects to a minimum. The machine first cleans the molds using a high pressure water wash to remove any fine contaminates on the molds. Each layer of the stack is coated onto a glass mold using the spin coating technique, which is a simple and efficient method for depositing uniform thin films on a substrate. The well understood technique controls the layer thickness by balancing the centrifugal forces of a developing thin film to the viscous forces that increase as evaporation takes place (Meyerhofer 1978; Bornside, Macosko et al. 1989). The repeatability of this method is extremely high as long as the coating environment is controlled such that the solvent evaporation rate stays constant. This is accomplished by regulating the room temperature of the coating chamber and also by exhausting solvent rich air out of the coating bowl.

After the solvent is evaporated a thin film on the order of a ¼ wavelength of a UV-curable monomer and nanoparticles remain. The layer is then partially cured using a pulse Xenon UV source lamp (the intensity is higher than a germicidal light), leaving an under-cured polymer nanoparticle composite. Subsequent layers are then added on top of the previous layer to build the anti-reflective stack in reverse order. Each mold is processed through the machine in about ten minutes.

The reverse coated molds are then assembled as shown in Figure 2.11 and a low viscosity monomer is introduced into the system. The monomer is then cured to form a lens plate using a UV source and heat. The curing process takes a total of 10 minutes. During this time the curing of the anti-reflective layers is completed which creates a very good bond between the layers and the polymer lens. When the cure is complete the molds are removed in a water bath and the lens is cleaned and placed into a low temperature oven and annealed. The final product has the surface qualities of the
mold itself, such that the article does not need any post processing to complete the prescription. This method using polymer nanocomposites is repeatable and a low cost solution to make AR lenses.

2.4 Nanocomposite characterization

Characterization of chemical and physical properties is critical for fabricating the nanocomposite coatings. The most common instruments needed are listed in Table 2.3. Among them, real-time FTIR is an important tool to monitor the UV polymerization process. There are three infrared recording methods used in this study: DRIFTS, transmission FTIR and ATR FTIR. DRIFTS, Diffuse reflectance FTIR, is mainly used to acquire the spectra of the surface chemistry of metal oxide nanoparticles. Conventional transmission FTIR is used for monitoring the [C=C] conversion rate for the kinetics of an UV polymerization. Since the nature of very fast reactions of acrylic UV polymerization, a real-time FTIR which is capable of recording a spectrum in a millisecond scale is desired. ATR FTIR is used for the surface chemistry of a plastic flat. X-ray diffractometer is useful for characterizing the crystal structure of metal oxide nanoparticles, which is closely related to the mechanical properties and refractive index.
Figure 2-9  AR lens assembly mold (the cut away shows the cavity into which the low viscosity monomer is added) (Courtesy of ODC)
Table 2-3 Characterization methods for fabricating the nanocomposite coatings

<table>
<thead>
<tr>
<th>Characterization</th>
<th>Instrument</th>
<th>Model</th>
<th>Application</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Chemical</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>FTIR (Transmission / DRIFS / ATR)</td>
<td>Mattson Galaxy</td>
<td>Series 3000</td>
<td>Kinetics of polymerization</td>
</tr>
<tr>
<td></td>
<td>ThermoNicolet</td>
<td>Model 470</td>
<td></td>
</tr>
<tr>
<td>X-ray photoelectron spectroscopy (XPS)</td>
<td>VSW (Al-Ka x-ray source)</td>
<td></td>
<td>Surface chemistry of metal oxide nanoparticles</td>
</tr>
<tr>
<td><strong>Mechanical</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nanoindentation / Nanoscratching test</td>
<td>Hysitron</td>
<td>TriboScope</td>
<td>Modulus, Hardness, Stiffness, Elastic/Plastic recovery, Adhesion, Fracture</td>
</tr>
<tr>
<td>Microindentation / Microscratching test</td>
<td>MicroPhotonics</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Microscopy</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Atomic Force Microscope (AFM)</td>
<td>Digital Instrument</td>
<td>Quesant</td>
<td>Topography of the coating surface</td>
</tr>
<tr>
<td>Profilometer</td>
<td>Ambios Technology</td>
<td>XP-1</td>
<td>Coating thickness</td>
</tr>
<tr>
<td>X-ray Diffractometer</td>
<td>Simens</td>
<td>D5000</td>
<td>Type and crystalinity of Metal oxide nanoparticles</td>
</tr>
<tr>
<td>SEM</td>
<td>Hitachi</td>
<td>S900</td>
<td>Fractures induced by nanoindentation and nanoscratching tests</td>
</tr>
<tr>
<td>SEM (EDS)</td>
<td>Simens</td>
<td>S3200</td>
<td></td>
</tr>
<tr>
<td>TEM (HRSEM / STEM / EELS)</td>
<td>JOEL</td>
<td>2010F</td>
<td>Particle size and cross section of AR coatings</td>
</tr>
<tr>
<td>TEM (HRSEM / STEM)</td>
<td>Simens</td>
<td>2000</td>
<td></td>
</tr>
<tr>
<td><strong>Optical</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>UV-Vis</td>
<td>HP</td>
<td>Hewlett Packard 8453</td>
<td>UV absorption</td>
</tr>
<tr>
<td>Refractive &amp; haze meters</td>
<td>Haze-Gard</td>
<td>BYK Gardner Haze-Gard Plus</td>
<td>AR reflectance and transparency</td>
</tr>
<tr>
<td><strong>Others</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PSD analyzer</td>
<td>Brookhaven</td>
<td>90 Plus</td>
<td>Size of metal oxide nanoparticles and the dispersion</td>
</tr>
</tbody>
</table>
XPS (X-ray photoelectron spectrum), or ESCA (electron spectrum of chemical analysis), is a powerful tool for the surface chemistry studies. The principle is to collect and analyze photoelectrons escaped from inner-shell electrons of atoms at the material surface (a few nanometer deep) under X-ray irradiation. The kinetic energy of the emitted photoelectron is characteristic of the binding energy of a particular shell of an atom and is unique for each element. The elemental composition is thus determined and is expressed in atomic percent units for the elements detected. The detected photoelectrons also provide identifying information of the element in which chemical groups.

AFM is the most convenient way to see the topography quality and the fracture features, but it should be cautious that the nature of this method may not see the real and detail morphology of a coating, such as the cracking, which can be seen under a SEM. Profilometer is convenient for measuring the coating thickness and the surface roughness. TEM is useful for obtaining a rich amount of information: (1) to double check the size of a metal oxide nanoparticle size with the result by a particle size analyzer, (2) to observe the dispersion quality of metal oxide nanoparticles (a dried sample made from a suspension on carbon coated cooper grids) and (3) to analyze the composition of an ultrathin nanocomposite coating by EELS and observe the particle dispersion (a cross-section sample needs to be prepared by using a diamond knife with a microtome at about -80°C, and then put on carbon coated copper grids).

Particle size analyzer is a very valuable tool for the particle size and distribution measurements and their dispersion quality evaluation. Since the measurement is based on the light scattering principle and a built-in mathematic model used for interpreting the data, besides, the input testing parameters, such as viscosity and refractive index, sometimes are not available accurately, therefore, a cross-check by a second characterization method is preferred.

UV-Vis spectrometer can be used to measure the UV absorption of a material, and then calculating the extinction coefficient $\varepsilon$ as shown in Equation 2.1 and Equation 2.2. For an UV absorption measurement, the sample needs to be dissolved or suspended in a low UV absorption solvent and contained in a fused silica cuvette with a known optical path-length, or to be formed a film on a low absorption silica substrate.
The absorption of a sample was obtained after the subtraction of the background absorption by the solvent or the substrate used. BYK Haze Gard measures optical transparency and refractive index of an article.

Nanoindentation and nanoscratching tests are the most critical because they can not only directly measure the mechanical properties but also act as an overall evaluation tool to guide the material selection, curing conditions, nanoparticle loading and packing and the AR multilayer design. Since the mechanical characterization methods are so critical in this project and the academic interests for characterizing the nanoscaled polymeric coatings, nanoindentation and nanoscratching tests will be discussed in detail in the following chapter.

2.5 Unique behaviors of ultrathin polymeric films

In order to fabricate nanocomposite coatings, it is necessary to be aware of some unique behaviors of ultrathin polymeric films (O'Connell and McKenna; Alcoutlabi and McKenna 2005; Geng, Yang et al. 2005). For example, a widely reported phenomenon is the reduction or the increase in the glassy-rubbery transition temperature \( T_g \) (Ellison Christopher and Torkelson John; Reiter; Ellison, Kim et al. 2002; Ellison and Torkelson 2002; Alcoutlabi and McKenna 2005). The reason for this phenomenon is believed to be that polymer chains in ultrathin coatings may not be in an equilibrium state, due to the constraint from the substrate and the possible residual stress after polymerization (Alcoutlabi and McKenna 2005). Since the AR coatings have a thickness from 50 nm to 3000 nm, the physicochemical behaviors of these ultrathin coatings are interesting to know for academic and practical reasons.

This study on the glass transition temperature in an ultrathin film illustrated that the size effect at a free film surface causes a depression in \( T_g \), but the interaction between a constrained thin film and a substrate causes an increase in \( T_g \) (Alcoutlabi and McKenna 2005). \( T_g \) decreases near the free surface and the reduction can extend over a distance of 10-14 nm, but the magnitude of the reduction depends on the overall thickness of the film (Ellison, Kim et al. 2002; Ellison and Torkelson 2002); therefore, a gradient \( T_g \) in the film was found (Ellison and Torkelson 2003). For these reasons, a large decrease in \( T_g \) was reported for free standing thin polystyrene films (Forrest,
Dalnoki-Veress et al. 1996) (Forrest, Dalnoki-Veress et al. 1997; Dalnoki-Veress, Forrest et al. 2001), while only a small decrease or even an increase in $T_g$ for supported polystyrene thin films (Keddie, Jones et al. 1995; Wallace, van Zanten et al. 1995; Jain and de Pablo 2002).

Generally speaking, the shift of glass transition temperatures in ultrathin polymeric films is quite dependant on the material and the experiment method, namely, polymer chemistry (Keddie and Jones 1995; Keddie, Jones et al. 1995; Dalnoki-Veress, Forrest et al. 2001; Sharp and Forrest 2003; O’Connell and McKenna 2005), molecular weight (Forrest, Dalnoki-Veress et al. 1997), molecular conformation (McKenna 2003), substrate effect or interactions between the substrate and the film (Hartmann, Gorbatschow et al. 2002), free standing films or supported films (Forrest, Dalnoki-Veress et al. 1997; Dalnoki-Veress, Forrest et al. 2001), thickness (Hartmann, Gorbatschow et al. 2002), testing methods (Grohens, Hamon et al. 2001), sample preparation (Alcoutlabi and McKenna 2005) and stresses during spin-coating and UV curing. Therefore, a glass transition temperature of a polymer ultrathin film could decrease (Ellison, Kim et al. 2002; Ellison and Torkelson 2002; Ellison and Torkelson 2003), increase (Keddie and Jones 1995; Keddie, Jones et al. 1995), remain constant (Hall, Hooker et al. 1997; O’Connell and McKenna 2005) or even disappear (Alcoutlabi and McKenna 2005) depending on the above factors. Interestingly $T_g$, ultrathin PS films are the most often reported polymer having a reduction phenomenon (Ellison, Kim et al. 2002; Ellison and Torkelson 2002; Ellison and Torkelson 2003), while PMMA and PVAc demonstrated a stable or an increase in $T_g$ (Alcoutlabi and McKenna 2005). The existing theories of $T_g$ are unable to explain adequately the size effect, partially because the glass transition phenomenon itself is not fully understood yet (Alcoutlabi and McKenna 2005). Because the acrylic monomers studied in this work have a similar chemical structure as that in PMMA, the $T_g$ of the ultrathin nanocomposite coatings may not have a remarkable size effect.

$T_g$ is closely correlated to the mechanical properties of materials; that is, a reduced $T_g$ corresponds to lower mechanical properties. For this reason, the mechanical properties of ultrathin polymer films were investigated by indirectly monitoring the thermoviscoelastic response in terms of the size effect and the substrate
effect for spin-coated thin films (Reiter; Reiter 1994; O'Connell and McKenna 2005). The reported information is quite mixed. Some researchers found that the mobility of the molecules at the surface were similar to the bulk materials; therefore, \( T_g \) and the mechanical properties remain as the bulk material (Ge, Pu et al. 2000). However, others found that the mobility of the molecules at the free surface of thin films were enhanced; therefore, \( T_g \) and the mechanical properties decrease (Pu, Rafailovich et al. 2001; Teichroeb and Forrest 2003). A novel nanobubble inflation test (O'Connell and McKenna 2005) recently measured the mechanical properties and rheological properties in thin polymer films and found that a reduction of poly(vinyl acetate) (PVAc) a dramatic stiffening of the films in the rubbery plateau; therefore, \( T_g \) and the mechanical properties increase (O'Connell and McKenna 2005).

In this dissertation work, the size effect on the mechanical properties has been studied by a direct nanoindentation measurement with a series of coatings at the thickness from submicron to micron.

### 2.6 Summary

Nanocomposites have extraordinary properties resulting from the interfacial interactions and from synergism between the properties of the parent components. The nanocomposite coatings have been applied as scratch resistant coatings, anti-corrosion coatings and optical filters in optoelectronic systems.

An anti-reflective (AR) lens is typically a layered structure composed of multilayered AR coatings with the thickness varying from 50 nm to 3 \( \mu \)m on a lens substrate, usually a plastic plate at this time. An AR lens is traditionally made from ceramic coatings by a chemical vacuum deposition method. It is found that, while utilizing a plastic as the lens substrate, the mismatch in mechanical behavior between the ceramic coatings and the plastic substrate has caused problems. This dissertation introduces a new approach for fabricating AR lenses by an in mold spin-coating method, with the antireflective coatings made from polymer nanocomposites. These nanocomposite coatings are fabricated by the process of dispersing nanoscale inorganic composites in an acrylic monomer system, spin-coating on a lens substrate and then conducting an \textit{in-situ} UV polymerization.
Metal oxide nanoparticles were selected for mechanical reinforcement and refractive index engineering purposes. Besides the metal oxide nanoparticle size, dispersion and compatibility with the polymer matrix are being considered for optical applications. Monomers containing carbon-carbon double bonds can be cured using photoinitiators and UV light. The Sartomer family of monomers has between one to five carbon-carbon double bonds per molecule, different chain lengths between reactive units, and different constituents along the chain segments. UV curable multifunctional acrylic monomers give higher degrees of cross-linking, and more rigid polymers; however, monomers with lower functionality usually have lower viscosity, which is good for coating processing. The more ethoxy groups in a molecule, the more hydrophilic the monomer will be. Hydrophilic polymers can help the dispersion of metal oxide nanoparticles in alcohols, ketones, and water. Acrylic derivatives, such as acrylated epoxy, acrylated urethane, acrylated polyether and acrylated polyester monomers or oligomers, can be used for superior mechanical properties and adhesion strength to a substrate. The type of photoinitiator is often chosen to have a relatively high extinction coefficient in the region of the electromagnetic spectrum matching the output of the lamp source used. In addition, it should be capable of producing free radicals efficiently with high yield, and the generated free radicals are capable of rapidly initiating polymerizations.

There are some factors that greatly affect the kinetics of an UV polymerization process, such as monomer, photoinitiator, UV source, oxygen inhibition, coating thickness and filler screening effects. In the presence of oxygen, the UV polymerization rate is retarded and the maximum polymerization degree is reduced due to the oxygen inhibition effect. Oxygen molecules diffusing from the gas phase into a coating can quench the initiator and scavenge both the initiating and the polymer radicals. Since the oxygen molecules diffuse faster in a thinner coating than in a thicker coating, the oxygen interferes with UV polymerization more severely for a thinner coating than for a thicker coating.

Transitional metal oxide nanoparticles, such as TiO$_2$ and CeO$_2$, significantly absorb UV light at a wavelength less than 300 nm. Thus, the polymerization process with those photoinitiators, such as 1-hydroxy cyclohexyl phenyl ketone whose
dissociation is efficient at the wavelength of 256 nm, is retarded considerably. Because the UV intensity at the top surface of the coating is stronger than that at the bottom of the coating due to the screen effect of the fillers, a gradient in polymerization degree across the coating thickness could be produced.

The formulations and the processing conditions for AR coatings can be optimized in order to balance the mechanical properties and the adhesion strength, through the evaluation of nanoindentation and nanoscratching tests combining FTIR and other characterization methods.
Chapter Three: Nanoindentation and nanoscratch testing methods

3.1 Introduction

3.1.1 Traditional methods

Indentation techniques have been widely used for evaluating the mechanical properties of materials for about a century. In order to compare the hardness of irons and alloys, a Swedish metallurgist, Brinell, created a method to force a smooth hard steel ball into a material surface for a fixed period of time and then measure the imprint area (Brinell 1900; Tabor 1996). This so-called Brinell test was quickly adopted as a general industrial method for comparing the plastic properties of materials, because of its easy operation and its straightforward understandable principles.

In the first half of the twentieth century, many scientists and engineers developed methods for measuring a broad range of the hardness of materials by using different indentation loading procedures, using various geometrical indentations and using hard indenter materials like diamond (Tabor 1951). The most famous ones were the Rockwell test with a spherical indenter and the Vickers test with a square-based pyramid indenter (Tabor 1951). The calculated hardness numbers were based on the residual indentation imprint area and assumed no elastic recovery of the materials. The imprint area of the indentation was generally in a large scale and easy to be measured optically.

3.1.2 Modern methods

With developing various microstructural and nanostructural devices, there is an increasing need to evaluate the material by applying a small load on an object in micro-/nano-scales. The latest technologies made it possible to build various microindentation and nanoindentation instruments, such as Microphotonics Microindenter (Micro Photonics Inc., Allentown, PA, USA), Hysitron Nanoindentation (Hysitron, Inc., Minneapolis, MN, USA), MTS Nano Indenter® XP (MTS Cooperation, TN, USA) and a NanoTest 600 (Micro Materials Ltd., Wrexham, UK). A schematic indentation instrument
reproduced with the permission of Microphotonics is shown in Figure 3.1. The depth and load resolutions of nanoindentation systems are usually at least 1 μN and 0.1 nm, respectively (Liu, Chen et al. 2003). Some of the instruments are capable of controlling the applied load at a nanoNewton scale and the displacement in a tenth of a nanometer.

However, it is difficult to measure the residual imprint of the indentation by a traditional optical method as the indenter produces a very small deformation under an extremely tiny load. A method to estimate the residual imprint area and the contact area between an indenter and an indented material was developed by Oliver and Pharr in the 1970s (Oliver and Pharr 1992).

A breakthrough was to realize that it is feasible to observe the material’s elastic response by controlling the unloading process as well (Bulychev, Alekhin et al. 1975). This is based on the phenomena that the initial unloading is primarily an elastic recovery. The fundamental understanding for this type of elastic contact was mainly developed by the studies of Hertz (Hertz 1896), Boussinesq (Boussinesq 1885) and Sneddon (Sneddon 1951).

In the past three decades, microindentation and nanoindentation methods have been extensively modified (Loubet, Georges et al. 1984; Doerner, Gardner et al. 1986). These studies were focused on accurately estimating the contact area taking into account of the nature of the material and the substrate effect. The analyses will be briefly summarized in the following sections. Today, microindentation and nanoindentation methods are widely applied for studying micro- and nano-mechanical properties of materials.
Figure 3-1  Instrument of Indentation (Courtesy of Microphotonics™)
3.1.3 Analysis of thin coatings.

Another active research focus is how to measure the properties of thin coatings. For a thick coating, it is sometimes possible to detach the coating from the substrate first and then test the “free standing” coating’s properties directly (Hutchinson and Suo 1992; Pharr and Oliver 1992). However, it is usually not practical to detach a thin or ultrathin coating from a substrate. The convenient way to test a thin coating is to apply a very small load and deform the coating on a very small scale in order to minimize the substrate influence, which usually requires using nanoindentation testing (Pharr and Oliver 1992) (Oliver and Pharr 1992; Fischer-Cripps 2002). This approach works well for a compliant coating on a stiff substrate, but may not be applicable for a stiff coating on a compliant substrate. The general method to deal with this problem is to try to extract the properties of a coating from the substrate effect by developing various analytical and empirical models (Doerner and Nix 1986; Malzbender, den Toonder et al. 2002) (Hsueh and Miranda 2004; Hsueh and Miranda 2004) (Gao, Chiu et al. 1992) (Berasategui, Bull et al. 2004).

3.1.4 Effect of layering order

Although many of these models were reported quite successful for the case of a compliant coating on a stiff substrate (Doerner, Gardner et al. 1986; Korsunsky, McGurk et al. 1998; Saha and Nix 2002; Tsui, Ross et al. 2003; Hsueh and Miranda 2004); the many attempts to develop analytical solutions for the case of a stiff coating on a compliant substrate have not been as successful as for the case of a compliant coating on a stiff substrate (King 1987; Gao, Chiu et al. 1992; Tsui, Vlassak et al. 1999; Kramer, Volinsky et al. 2001; Beegan, Chowdhury et al. 2004; Berasategui, Bull et al. 2004; Ni and Cheng 2005).

Many of the models to separate the elastic modulus of the stiff coating from the compliant substrate are only applicable for specific coating-substrate systems. For example, when the coating and the substrate are nearly plastically homogeneous, the “intrinsic” coating modulus can be extracted from the data by using the material “characteristic parameter,” the ratio of load to the square of unloading stiffness ($F/S^2$)
(Joslin and Oliver 1990; Saha and Nix 2002). Usually other factors such as the interfacial adhesion strength (Wu, Moshref et al. 1990; Tsui, Ross et al. 1997), residual stress (Ghaffari, Wang et al. 1996; Hsueh 2003) and fracture of the coatings (debonding or cracking)(McGurk and Page 1997; Korsunsky, McGurk et al. 1998; Beegan, Chowdhury et al. 2004) have not been integrated into the models. There are no existing models in literature specifically developed for an ultrathin polymeric coating on a more compliant substrate. One of the aims of this dissertation work is to examine the validity of several potential models for a single-layered stiffer nanoscale densely cross-linked polymeric coating on a more compliant acrylic substrate.

3.2 Elastic modulus measurements by nanoindentation testing

For a viscoelastic material such as polymer, a typical indentation experiment has the following steps: (1) the material surface is indented with a known geometry tip at a specified load and a controlled rate, (2) the indentation is stopped at a specific load (or distance) and the tip is held at this position for a period of time, and then (3) the sample is unloaded at a controlled rate (Geng, Yang et al. 2005). This experimental procedure is illustrated in Figure 3.2(a). During indentation, the force $F$ and the indenter penetration depth $\delta$ are recorded as a function of time. Thus, a load-displacement curve is obtained as shown in Figure 3.2(b). The recorded load-displacement curve could be divided into three stages corresponding to the three-stage loading procedure: (1) during the loading stage, the indenter keeps penetrating into the indented material, (2) during the holding stage, the indenter continuously moves inside the material if the material is viscoelastic in nature, a phenomenon called "creep", and then (3) during the unloading stage, the indenter rebounds back due to the material’s elastic recovery from a deformation. In the load-displacement curve, $\frac{dF}{d\delta}$ is the unloading stiffness (the slope of the initial unloading curve), $\delta_{\text{max}}$ is the maximum indentation penetration depth, $\delta_e$ and $\delta_p$ are the elastic and plastic indentation depths respectively, $\delta_{\text{creep}}$ is the distance of the indenter moving further into the material during the holding stage and $\delta_c$ is the indentation contact depth between the indenter and the indented material at the maximum indentation depth. The exact position of $\delta_c$ depends on the indenter geometry.
and the indented material. A number of the sample’s mechanical properties can be derived from the load-displacement curve using empirical, numerical and analytical models (Oliver and Pharr 1992), which will be discussed in the following sections.

Figure 3.3 shows typical indentation load-displacement curves of a 47 nm SR399 polymeric coating on a silicon wafer substrate. SR399 is a penta-functional acrylic monomer that can be cured to form a densely polymeric network under an UV radiation. The detailed curing conditions for fabricating these coatings were introduced in Chapter Two. The indentation testing conditions were the loading and the unloading at 5 sec each, the maximum indentation load of 1 \( \mu \)N and holding for 2 seconds. These are the standard testing conditions applied for ultrathin SR399 coatings, which were set up based on the studies that will be reported in Chapter Four. In this dissertation, unless otherwise stated, the indentation experiments were conducted using this standard procedure by varying the maximum indentation loads. From Figure 3.3, since these curves of different runs (three individual tests at three locations on the coating surface) are very repeatable even at the indentation load of 1 \( \mu \)N, it is clear that the indentation tests on nanoscale polymeric coatings are well controlled and the results are reliable.
Figure 3-2  (a) A typical indentation load profile for polymer and (b) its indentation load-displacement curve
Figure 3-3  The load-displacement curves of a 47 nm SR399 coating at 1uN holding 2 s
(Three tests were conducted at three different locations on the coating surface)
3.2.1 Classic models for a half space elastic material

The classic model was originally generated based on Hertz’s solution (Hertz 1896), which assumed that a spherical indenter indents a half-space material, no cracks and no plastic deformation occur and the material indented behaves in a “sink-in” fashion as shown in Figure 3.4. ”Sink-in” means the real indentation contact depth $\delta_c$ is smaller than the maximum indentation depth $\delta_{\text{max}}$. These assumptions are only valid if the ratio of the contact radius $a$ to the indenter radius $R$ is small enough.

3.2.1.1 Load vs. indentation depth

Hertz found the relationship between the indentation load $F$ and the indentation penetration depth $\delta$ and the material mechanical properties as below (Hertz 1896).

$$F = \frac{4}{3} R^{0.5} E_r \delta^{3/2}$$  \hspace{1cm} 3.1

In which, $E_r$ is the reduced elastic modulus that including the response of the indented material and the indenter during the indentation. The properties of the indented material can be calculated by (Oliver and Pharr 1992):

$$\frac{1}{E_r} = \frac{1-\nu_i^2}{E_i} + \frac{1-\nu_s^2}{E_s}$$  \hspace{1cm} 3.2

where $E_i$ and $\nu_i$ are the elastic modulus and the Poisson’s ratio of the indenter material respectively, and $E_s$ and $\nu_s$ are the elastic modulus and the Poisson’s ration of the indented material respectively.

Applying Equations 3.1 and 3.2, the elastic modulus of the material can be obtained in the case of a spherical indenter indenting a half-space system.
Figure 3-4 A “sink-in” phenomenon of an indented half-space material
3.2.1.2 Modulus vs. indentation depth

When using a sharp indenter, a plastic deformation of the indented material usually is inevitable. Malzbender, et al. found a relationship between the indentation load $F$ and the indentation depth $\delta$ and the material mechanical properties at the loading stage (the loading part of the load-displacement curve) (Malzbender and de With 2000) (Malzbender, De With et al. 2000). The Equation 3.3 of this relationship is applicable for an infinitely sharp indenter, such as an ideal Berkovich or Vickers’ indenter.

$$F = \left[ \frac{1}{\sqrt{24.5}} E_r \delta^2 \right] \left\{ E_r + \varepsilon \left[ \frac{\pi}{4} \frac{H}{E_r} \right]^2 \right\}$$  \hspace{1cm} 3.3$$

in which $\varepsilon$ is a constant related to the geometry of the indenter used. Typical $\varepsilon$ values are 0.75 for a paraboloid and 0.72 for a conical indenter. Berkovich and cubic corner indenters common use 0.75 for $\varepsilon$ (Oliver and Pharr 1992) [Hysitron’s technical support]. $H$ is the hardness of the material. From Equation 3.3, either $E_r$ or $H$ can be calculated if either one is known.

3.2.1.3 Modulus vs the unloading curve

Nowadays, the most popular method to calculate the modulus from the indentation load-displacement curve is analysis of the unloading curve. The widely accepted concept is that the initial recovery of the unloading is purely elastic no matter whether the material had plastic deformation during the loading processing. Based on Sneddon’s work, Oliver and Pharr proposed the classic modulus model as below (Oliver and Pharr 1992).

$$E_r = \frac{\sqrt{\pi}}{2\sqrt{A}} \frac{dF}{d\delta}$$  \hspace{1cm} 3.4$$

Here, $F$ is the peak indentation load, $\delta$ is the indentation penetration depth, and $\frac{dF}{d\delta}$ is the tangent to the upper portion of the unloading curve or the unloading stiffness. $A$ is the contact area between the film and the indenter. The value of $A$ is hard to be
precisely estimated because the profile of the indented material could be either “sink-in” or “pile-up” depending on the nature of the material. Some indented material profiles, presenting either “sink-in” or “pile-up” phenomena. Two examples are shown in Figure 3.5. The sample with a “sink-in” deformation, in Figure 3.5(a), is a 350 nm ceramic AR coating on a plastic substrate; the test was conducted at an indentation load of 2000 μN. The sample with a “pile-up” fashion, in Figure 3.5(b), is a 125 nm polymeric SR399 coating on a plastic substrate; the test was conducted at an indentation load of 500 μN. It is obvious that a ceramic material responds differently from a polymeric material under an impression force.
Figure 3-5  AFM images of the indentation profiles: (a) “sink-in” for a ceramic coating and (b) “pile-up” for a polymeric coating on the plastic lens substrates
3.2.1.4 Effect of indentation depth on measured properties

In a coating-substrate system, the elastic response of indentation is usually a combination of the coating and the substrate. It is predictable that the coating material dominates the laminate response at a lower indentation load or a shallower indentation depth, and the substrate property dominates at a larger indentation load or at a deeper indentation depth. This is because the elastic deformation volume underneath the indenter becomes larger at a larger indentation load and a deeper indentation penetration depth. The influence of the substrate depends on the material properties of both coating and substrate (modulus and hardness), coating thickness, indentation load or penetration depth and indentation geometry and tip radius (Malzbender, den Toonder et al. 2002). A sharper indenter with a smaller tip radius induces a smaller stress field within the indented material, and thus the substrate effect is minimized. For this reason, it is preferred to measure the coating’s properties by using a sharper indenter such as a cubic corner indenter.

3.2.2 Models for elastic modulus in a coating-substrate system

In the case that the overall elastic response of an indentation is a combination of the coating and the substrate properties, there are various models to try to estimate the coating properties alone from the substrate effect. Some of the potentially applicable models for an ultrathin coating-substrate system are summarized as below.

3.2.2.1 Doerner and Nix Empirical model

One of the early empirical model proposed by Doerner and Nix as (Doerner and Nix 1986):

\[
\frac{1}{E^*} = \phi_{DN} \frac{E_c}{E_c} + 1 - \phi_{DN} \frac{E_s}{E_s}
\]

Where, \( E^* \) is the apparent (composite) modulus combining the properties of the coating and the substrate, \( E_c \) and \( E_s \) are the moduli of the coating and the substrate respectively, and the weight function \( \phi_{DN} \) is given as (Doerner and Nix 1986):

\[
\phi_{DN} = 1 - \exp\left(-\frac{\beta^*t}{\delta}\right)
\]
In which, \( t \) is the coating thickness, \( \delta \) is the indentation depth, and \( \beta \) is a constant which is related to the coating thickness (Malzbender, de With et al. 2000) (King 1987). This model was successfully applied for a compliant sol-gel coating on a stiff glass substrate (Broek 1997; Malzbender, de With et al. 2000). The accuracy of the model becomes worse at a lower indentation load when the elastic response is dominated by the coating (Malzbender, de With et al. 2000) (Malzbender, de With et al. 2000).

3.2.2.2 Hsueh and Miranda’s model using a spherical indenter

For a spherical indenter and at Hertzian indentation conditions (i.e. a pure elastic contact between the tip and the indented material) and when the coating is infinitely thick, the corresponding indenter displacement \( \delta_\infty \) is given by (Johnson 1985),

\[
\delta_\infty = \left[ \frac{9(1-\nu_c^2)F^2}{16RE_c^2} \right]^{1/3} \tag{3.7}
\]

where the subscription “\( \infty \)” means the infinite thickness of a coating, \( F \) is the maximum load, \( \nu_c \) is the coating’s Poisson ratio, \( E_c \) is the coating modulus and \( R \) is the radius of a spherical indenter.

When a coating is not infinitely thick but has a thickness of \( t \), and if the substrate is stiffer than the coating, Waters (Waters 1965) suggested that the overall displacement \( \delta \) is related to \( \delta_\infty \) as a function of the coating-thickness-to-contact-radius ratio, \( t/a \). Hsueh and Miranda (Hsueh and Miranda 2004; Hsueh and Miranda 2004) extended this argument to the compliant substrate case and claimed that the overall indentation displacement is related to both \( t/a \) and the coating-to-substrate Young’s modulus ratio \( E_c/E_s \) as below.

\[
\delta = \delta_\infty \alpha^{-2/3} \tag{3.8}
\]

where,

\[
\alpha = \left( 1 + \frac{E_s(1+\nu_s)}{\pi E_c(1-\nu_c^2)}[(3-2\nu_s)\lambda_1 + \lambda_2] - \frac{1}{\pi(1-\nu_c)}[(3-2\nu_c)\lambda_1 + \lambda_2] \right)^{-1} \tag{3.9}
\]
In which, \( \nu_s \) and \( E_s \) are the Poisson ratio and the Young’s modulus of the substrate respectively. \( \lambda_1 \) and \( \lambda_2 \) are the functions of \( t/a \). \( a \) is the contact radius between the tip and the surface of the indented material.

\[
\lambda_1 = \frac{\pi}{2} \left(1 + \frac{t^2}{a^2}\right) - \frac{t}{a} \sin^{-1} \left[ \frac{t}{a} \left(1 + \frac{t^2}{a^2}\right)^{-1/2} \right]
\]

\[
\lambda_2 = -\frac{\pi}{2} \left(1 + \frac{3t^2}{a^2}\right) + \frac{3t}{a} + \left(1 + \frac{3t^2}{a^2}\right) \sin^{-1} \left[ \frac{t}{a} \left(1 + \frac{t^2}{a^2}\right)^{-1/2} \right]
\]

The analytical model was reported to agree well with the finite element results at a certain range of the ratio of \( E_c \) to \( E_s \) and the ration of \( a/R \). Hsueh and Miranda found that the accuracy of the model became worse when the Equation 3.8 applied to the case of a stiff coating on a compliant substrate, compared with the reverse case. The method was developed based on a macro-scale coating-substrate system and has not yet been verified for an ultrathin coating (Hsueh and Miranda 2004).

### 3.2.2.3 Gao’s model using a conical indenter

The Gao’s model was set up based on the relationship that the unloading compliance \( \frac{d\delta}{dF} \) (the inverse unloading stiffness) is linearly dependent on the inverse of the plastic indentation depth \( \frac{1}{\delta_p} \) by a material constant \( \frac{1-\nu}{\mu} \), where \( \nu \) is the Poisson ration and \( \mu \) is the shear modulus (Loubet, georges et al. 1984). When a coating-substrate system deforms both elastically and plastically under a conical indenter, the unloading compliance \( \frac{d\delta}{dF} \) has a relationship with the plastic depth \( \delta_p \) (Gao, Chiu et al. 1992).

\[
\frac{d\delta}{dF} = \frac{1}{4\delta_p \tan \theta} \left( \frac{1-\nu}{\mu} \right)_{\text{eff}}
\]

\[
\mu = \frac{E}{2(1+\nu)}
\]
where, $\theta$ is the half enclosed angle of a conical indenter, $\nu$ is the Poisson ratio and $\mu$ is the shear modulus. The subscript $\text{eff}$ means the overall “effective” response of the coating-substrate system during the indentation. The effective response can be related to the respective properties of a coating and a substrate as below.

$$\left(\frac{1-\nu}{\mu}\right)_{\text{eff}} = \frac{1-\nu_\text{c}-(\nu_\text{c}-\nu_\text{s})I_\text{c}(t/a)}{\mu_\text{s}+(\mu_\text{c}-\mu_\text{s})I_\text{s}(t/a)}$$  \hspace{1cm} 3.13

Where, the subscripts of $c$ and $s$ denote the coating and the substrate respectively. $I_\text{c}$ and $I_\text{s}$ are functions of the coating-thickness-to-contact-radius ratio $(t/a)$. $t$ is the coating thickness and $a$ is the contact area. Let $\xi = t/a$, then,

\begin{align}
I_\text{c}(\xi) &= \frac{2}{\pi} \arctan \xi + \frac{\xi}{\pi} \ln \frac{1+\xi^2}{\xi^2} \hspace{1cm} 3.14a \\
I_\text{s}(\xi) &= \frac{2}{\pi} \arctan \xi + \frac{1}{2\pi(1-\nu)} \left[ \xi(1-2\nu) \ln \frac{1+\xi^2}{\xi^2} - \frac{\xi}{1+\xi^2} \right] \hspace{1cm} 3.14b
\end{align}

Each side of Equation 3.11 is times the coating thickness $t$, then,

$$\frac{d\delta}{dF} t = \frac{t}{4\delta_p \tan \theta} \left(\frac{1-\nu}{\mu}\right)_{\text{eff}}$$  \hspace{1cm} 3.15

The value of $\frac{d\delta}{dF} t$ can be calculated as a function of $\frac{t}{\delta_p}$ according to Equation 3.15. The moduli of the coating and the substrate can be calculated from the slope of the plot between $\frac{d\delta}{dF} t$ and $\frac{t}{\delta_p}$ by using Equation 3.13.

### 3.2.2.4 Korsunsky’s empirical model using a sharp pyramidal indenter

Originally, Korsunsky and his colleagues (Korsunsky, McGurk et al. 1998; Tuck, Korsunsky et al. 2001) set up a model for the effective hardness of a coating-substrate system as a function of the relative indentation depth $\beta$ and the hardness of a coating and a substrate. $\beta$ is the indentation depth normalized with respect to the coating thickness. This model was developed by considering various factors, such as the deformation types of the coating-substrate system, possible cracking of the coatings (B.Jonsson 1984; Bull and Rickerby 1990; McGurk and Page 1997; Korsunsky, McGurk...
et al. 1998), the coating thickness and the mismatch of hardness between a coating and a substrate. The proposed model is

\[ H_{sys} = H_s + \frac{H_c - H_s}{1 + \beta^2 \frac{t}{\phi}} \]

where \( H_{sys} \), \( H_c \) and \( H_s \) are the effective hardness of the coating-substrate system, the coating hardness and the substrate hardness respectively, \( t \) is thickness of the coating, \( \phi \) is a parameter that may relate to the coating fracture (Korsunsky, McGurk et al. 1998).

Compared with the hardness, the elastic modulus is more prone to be affected by the substrate at a shallower indentation depth due to the longer range of the stress field effect (Saha and Nix 2002). The above model was not expected to fit the elastic modulus data. However, the model originally developed for the hardness has been adopted in the same form for the effective elastic modulus interpretation and has been reported fairly successfully for a single-layer and even a double-layer coating-substrate system, although there was lack of soundly-based physical origins (Berasategui, Bull et al. 2004). The adopted model for the composite modulus \( E_{sys} \) is

\[ E_{sys} = E_s + \frac{E_c - E_s}{1 + \beta^2 \frac{t}{\phi}} \]

where \( E_{sys} \), \( E_c \) and \( E_s \) are the effective elastic modulus of the coating-substrate system, the coating elastic modulus and the substrate elastic modulus respectively, \( t \) is thickness of the coating, \( \phi \) is a parameter that may relate to the coating fracture and \( \beta \) is a fitting parameter.

### 3.3 Other properties from nanoindentation experiments

The most important advantage of nanoindentation is that a wealth of information can be derived from a single test. The mechanical properties that can be studied by a nanoindentation test are hardness, residual stress, creep, coating fracture toughness, interfacial fracture toughness (or adhesion energy) and others (Pharr and Oliver 1992; Malzbender, de With et al. 2000; Malzbender, de With et al. 2000; Fischer-Cripps 2002).
3.3.1 Hardness

The indentation testing was originally developed for the hardness measurement of an indented material. Hardness is a measurement of a plastic deformation of a material under impression. The area of the residual imprint after removing the indentation load is related to the plastic deformation. Hardness is thus defined as the ratio of the maximum load $F$ to the residual imprint area $A$ (Oliver and Pharr 1992):

$$H = \frac{F}{A} \quad \text{(3.18)}$$

The residual imprint area $A$ can be estimated from an indentation load-displacement curve, or calculated from the calibrated indenter tip area function.

Unlike the elastic modulus, hardness $H$ is not an intrinsic property of a material although it is related to material properties such as the yield strength $Y$ and elastic modulus $E$ (Malzbender, den Toonder et al. 2002). The relationship between these properties is dependant on the indenter geometry and other factors (Yu and Blanchard 1996; Cheng and Cheng 1998; Malzbender, den Toonder et al. 2002). For metals, the hardness $H$ of a material is estimated approximately from the yield strength $Y$, (Tabor 1951):

$$H = 2.8Y \quad \text{(3.19)}$$

There are other factors such as indenter tip radius effect that affect the accuracy of hardness measurements. The plastic response is generally a combination of the properties of both the thin coating and the substrate. A similar treatment needs to determine the hardness of a coating in a coating-substrate system as for the modulus in a coating-substrate system. In this dissertation, the elastic modulus is chosen as the key mechanical property of a coating-substrate system, although hardness was also studied during the research work.

3.3.2 Fracture toughness

Materials especially for brittle materials tend to fracture under sufficient loads (Cook and Pharr 1990). For a sharp indenter, the fracture is often initiated as a crack (Lawn and Evans 1977; Pharr, Harding et al. 1993; Harding, Oliver et al. 1995; Malzbender and Steinbrech 2003). The fracture toughness, $K_I$, a characteristic
property of a material, is the stress intensity associated with an advancing crack with a process-zone (Li, Palacio et al. 2002). Lawn and Evans derived a relationship between the fracture toughness $K_c$ and the critical load for the crack initiation $F^*$ when using a Vickers indenter on a monolithic material (Lawn and Evans 1977):

$$F^* = 21.7 \times 10^3 \frac{K_c^4}{H^3}$$

This equation is also valid for a Berkovich indenter (Malzbender, den Toonder et al. 2002) because the projected contact area between the indenter and the surface of the indented material is the same as the Vickers indenter at an equal indentation depth (Oliver and Pharr 1992).

Another fundamental parameter is the fracture energy, $\Gamma$, which the resistance to crack propagation. Griffith (A.A.Griffith 1921) derived the relation between the fracture toughness and the fracture energy as,

$$\Gamma = \frac{K_c^2}{E}$$

where, $E$ is the modulus of the materials. The $E$ can be replaced with the effective modulus for the coating-substrate systems, $E^*$.

The fracture studies for layered systems are more complicated than monolithic materials because of the difficulty in defining the stress field across the interface between the layers. For example, the approximation of the crack in a semi-circular shape (the depth of the crack is equal to the half of crack length) is not accurate. Also, delamination, not fracture, is a common failure mode for coating-substrate systems.

Different techniques have been developed to evaluate the interfacial strength of surface coating, such as blister tests (Williams 1970; Bennet, Devries et al. 1974; Jensen and Thouless 1993), residual stress-driven delamination tests (Bagchi, Lucas et al. 1994), scratch tests (Huang, Lu et al. 2004; Wirasate and Boerio 2005) (Zhang, Tsou et al. 2002; Ramsteiner, Jaworek et al. 2003) and indentation tests (Marshall and Evans 1984; Matthewson 1986; Dehm, Ruhle et al. 1997; Vlassak, Drory et al. 1997; Li, Carter et al. 2001; Li, Palacio et al. 2002; Lu and Shinozaki 2002). The scratch test is a very popular technique for qualitatively determining the adhesion of various coatings, although it may not provide an absolute measurement of the interfacial strength for the
coating-substrate interface (Kriese, Gerberich et al. 1999). Both the blister test and residual stress-driven delamination test require complicated sample preparation and are often limited to surface coatings with poor adhesion, i.e. no surface cracking occurs during test (Vlassak, Drory et al. 1997).

The indentation-induced delamination of a coating from a substrate can be initiated by pushing a rigid indenter through the coating plane. In some indentations, significant deformation is created only in the coating, while in others plastic deformation is also introduced in the substrate. During the loading portion of an indentation test, the change of the deformation behavior in a sample can be detected by sudden slope changes or discontinuities in the load-displacement curve. These are referred to as “pop-in” events or sudden displacement “excursions”, and have been reported for both material phase fracture and the indentation-induced delamination (Corcoran, Colton et al. 1997; Bei, Lu et al. 2004; Wang, Qiao et al. 2004). A typical “pop-in” event occurred while indenting a 125 nm SR399 coating on a compliant plastic lens substrate as shown in Figure 6.5. The delamination related “pop-in” events occurred at the indentation depth of 830 nm and the indentation load around 700 μN at different indentation tests independent of the applied indentation load. Therefore, the indentation technique is a well defined tool to study adhesion properties of laminate interfaces. For comparison, a complete “chipping” fracture which is often observed with a very brittle and poor adhesion ceramic coating as shown in Figure 3.6. This ceramic coating with a thickness of 350nm, fabricated by a vacuum deposition, was provided by ODC labeled as the sample “Foundation 2004 without hydrophobic layer”. Note that the “chipping” events also occurred at the a narrow range of indentation depth around 400 nm and the indentation load around 280 μN at different indentation tests independent of the applied indentation load. The indentation tests were conducted at different setting indentation loads of 200, 300, 400, 600, 800 and 1000 μN as shown in Figure 3.6(a) for the repeatability check and shown in Figure 3.6(b) for a close look of “chipping” at an indentation load of 800 μN. The indentation test conditions were loading and unloading 5 seconds each and holding at the maximum load 2 seconds.

Previous indentation-induced delamination studies focused on the relation between the indentation load and the delamination size. Chiang et al (Chiang, Marshall
et al. 1982) evaluated the interfacial strength between a surface coating and a substrate for the indentation using a Vickers indenter. They suggested that the indentation deformation compressed the coating, leading to the delamination of the coating from the substrate. Using the theory of linear fracture, Evans and Hutchinson (Evans and Hutchinson 1984), Marshall and Evans (Marshall and Evans 1984), and Rossington et al (Rossington, Evans et al. 1984) studied interfacial crack propagation to determine the resistance to interfacial delamination. Assuming indentation-induced elastoplastic deformation in the coating, Matthewson (Matthewson 1986) proposed that the radial displacement caused by indentation introduces a shear stress at the interface, which causes the initiation and propagation of adhesive failure. Ritter et al (Ritter, Lardner et al. 1989) developed a simple model for calculating fracture energy based on the indentation load versus the delamination size. Extending the analysis developed by Marshall and Evans (Marshall and Evans 1984), Kriese et al (Kriese, Gerberich et al. 1999) considered the indentation-induced delamination of multilayer structure and evaluated the effect of multilayer structure on the fracture toughness. Vlassak et al (Vlassak, Drory et al. 1997) developed a microwedge technique to measure the adhesion of brittle films to ductile films and obtained the fracture toughness as a function of the width of the delamination area.
Figure 3-6  A “chipping” event of a ceramic coating under an indentation stress (a) multiple tests at the setting indentation loads of 200, 300, 400, 600, 800 and 1000 μN, and (b) a single test at a setting indentation load of 800 μN.
Indentation-induced interfacial cracks propagate in the loading and unloading process. It is very difficult if even possible to determine exactly the size of the delamination zone. This is particularly true for non-brittle, elastic materials that may partially recoil after a delamination event. Thus, it would be useful to determine the interfacial strength from the indentation loading-unloading curve. Based on the shear lag model, Dehm et al (Dehm, Ruhle et al. 1997) developed an approximate elastic model for the estimation of the interfacial yield strength of a metal film on a ceramic substrate using a conical indenter. They neglected the effect of the deformation in the substrate and assumed that the contact between the film and the substrate was frictionless directly under the indentation. Extending the approach given by Dehm et al (Dehm, Ruhle et al. 1997) to the indentation of polymeric thin films of poly(methyl methacrylate), polystyrene and high impact polystyrene on a glass substrate using a flat-ended cylindrical indenter, Lu and Shinozaki (Lu and Shinozaki 2002) obtained a critical interfacial shear strength using the Tresca yield criterion. However, there are few studies on the indentation-induced delamination of a submicron polymeric coating on a polymeric substrate with similar elastic properties, which likely displays different behavior from soft coatings on hard substrates.

The dissertation will report the nanoindentation-induced delamination of submicron polymeric coatings on a polymeric substrate and evaluate the effect of the coating thickness. A quantitative evaluation of the interfacial strength is described. The indentation-induced delamination is analyzed relating the indentation load at the excursion in the loading curve to the critical interfacial shear stress at which the delamination initiates.

3.3.3 Others

Many other properties of the indented material can be obtained from the indentation load-displacement curve, such as elastic recovery, creep, viscoelastic property and thickness of the coating.

The elastic recovery could be defined as below,

\[
\text{Elastic recovery, } \% = \frac{\delta_c}{\delta_{\text{max}}}
\]

3.22
In which, $\delta_e$ and $\delta_{\text{max}}$ are the elastic recovery during the unloading stage and the maximum indentation depth respectively (see Figure 3.2(b)).

The elastic recovery is a good indication of the type of the material or the structure of the indented system. For example, the elastic recovery is 74% for a 3 $\mu$m SR399 coating, while it is about 40% for three submicron SR399 coatings, both on the same type of plastic plates, as shown in Figure 3.7. These coatings were spin-coated and UV cured on the acrylic plastic substrates at the same conditions. The indentation tests were conducted with the standard testing conditions as discussed in Section 3.2.

The thickness of a thin coating on a stiff substrate could be estimated from the slope changes from the loading part of the indentation load-displacement curve, especially in the case of a compliant coating on a stiff substrate. For example, the thickness of a SR399 coating can be estimated about 125 nm as the indenter hits its silicon wafer substrate as shown in Figure 3.8. Note that three curves of different runs at three different locations on the coating surface are very repeatable. The results estimated by an indentation are usually pretty consistent with the profilometer measurements.
Figure 3-7  The elastic recoveries were different for a micron coating from the submicron coatings in a polymer coating-substrate system.
Figure 3-8  The thickness of a coating can be estimated from the slope change of the indentation load-displacement curve.
3.4 Nanoindentation instruments and their calibration

The elastic modulus of an ultrathin coating can be measured by a nanoindentation. The nanoindentation tests were performed with a Hysitron TriboScope™ (Minneapolis, MN) attached to a Quesant (Agoura Hills, CA) atomic force microscope (AFM). A diamond NorthStar cubic indenter with a nominal tip radius of 40 nm (Minneapolis, MN) was used. The penetration depth and applied load were used to compute the modulus of the films.

3.4.1 Instruments

The main components of a TriboScope™ nanoindentation system are the transducer head and the 3D piezo actuator. The transducer is a three-plate capacitive force-displacement sensor which precisely measures the loads during an indentation test. 1D transducer is used for an indentation test and the capacity of maximum load is about 10,000 mN. An additional 2D transducer is equipped for a nanoscratching test which can measure the loads in the vertical direction and in the lateral direction simultaneously. The 3D piezo actuator controls the displacements in three dimensional directions and it is also a main part of the attached scanning probe microscope system (SPM) from Quesant™. The integrated AFM system greatly enhances the function of a nanoindentation because it allows the topography of material to be imaged before and after the indentation. As discussed previously, the imprint of an indentation contains important material information.

It should be pointed it out that the AFM images by this instrument are obtained through the scanning of the indenter probe (a contact mode), but a conventional AFM uses a cantilever as a probe. The advantages of a cantilever probe are: (1) much sharper tip (tip radius is less than 10 nm, but the indenter probe is 40nm –100 nm), (2) higher load sensitivity (small spring constant), (3) flexible for either contact or tapping testing modes and (4) lower cost (the material of cantilever such as SiN₄ is usually a ceramic, while the nanoindenter is diamond). Therefore, the resolution of an AFM image with a cantilever is better than that obtained with an indentation probe. In spite of this,
an AFM system is indispensable component for a nanoindentation system. The principle of a TriboScope™ system and the interface to SPM are shown in Figure 3.9.
Figure 3-9  Diagram of TriboScope interface to SPM
3.4.2 Calibration

3.4.2.1 Compliance of the instrument

During a nanoindentation test, the position of the indenter relative to the surface of a sample, or the indentation depth, is monitored simultaneously with the applying load as a function of time. The measured displacements are actually the sum of the indentation depth in the specimen and the deformation of the instrument itself, mainly coming from the transducer. This instrument influence is characterized as the load-frame compliance. The load-frame compliance needs to be measured because of its importance, especially at a large load.

The compliance is the inverse of the stiffness. The contact compliance of the axisymmetric indenter and an elastically isotropic half-space is given by:

$$C_c = \frac{d\delta}{dF} = \frac{\sqrt{\pi}}{2} \left( \frac{1}{\sqrt{A}} \right) \frac{1}{E_r}$$

where $\delta$ is the penetration depth, $F$ is the load, $A$ is the contact area (the projected area), $E_r$ is the reduced modulus described by the relationship,

$$\frac{1}{E_r} = \frac{1}{E_{\text{specimen}}} + \frac{1}{E_{\text{indenter}}}$$

where, $E$ is Young's modulus and $\nu$ is Poisson's ratio.

To account for elastic displacements of the compliance of the instrument, the instrument compliance, $C_m$ is added to the contact compliance $C_c$,

$$C_{\text{total}} = C_m + C_c = C_m + \frac{\sqrt{\pi}}{2} \left( \frac{1}{E_r} \right) \frac{1}{\sqrt{A}}$$

The nanoindentation hardness, $H$, is defined as,

$$H = \frac{F}{A}$$

Here, $F$ is the maximum applied force, and $A$ is the contact area at, therefore, the $C_{\text{total}}$ can be represented as,

$$C_{\text{total}} = C_m + C_c = C_m + \frac{\sqrt{\pi}}{2} \frac{\sqrt{H}}{E_r} \frac{1}{\sqrt{F}}$$
According to the Menu of the Hysitron TriboScope manual, it is a fair assumption that for Fused Quartz, the hardness and reduced modulus are constant at large indentation depths ($h_c > 1/3$ tip radius) and no cracks formed. Therefore, $\frac{1}{stiffness}$ vs. $\frac{1}{\sqrt{F_{\max}}}$ should have a linear relationship. The plot between them will yield a straight line and the intercept on the Y axis gives the machine compliance $C_m$. A typical testing result was 0.0008 nm/μN as shown in Figure 3.10. According to the technical support of Hysitron, the normal machine compliance is in the range of 0.0007 nm/μN to 0.0010 nm/μN, varying with the installation of the indenter and the environmental temperature. Besides, a sharper indenter could cause cracks with quartz at a very high indentation load, giving a wrong machine compliance data. The detailed procedure is attached in the Appendix B1.
The machine compliance by a calibration with quartz

Figure 3-10

Compliance($C_m$), nm/μN

\[ y = 1.2879x + 0.0008 \]

\[ R^2 = 0.9977 \]
3.4.2.2 Tip area function

In the equation 3.4, if the geometry of an indenter is perfect, the contact area \( A \) can be easily calculated from the indentation penetration depth \( \delta \) by the following relation (Oliver and Pharr 1992):

\[
\delta_c = \delta_{\text{max}} - \varepsilon \frac{F_{\text{max}}}{S_{\text{max}}}
\]

3.28

In which \( \delta_c \) and \( \delta_{\text{max}} \) are contact indentation depth and the maximum indentation depth respectively, \( F_{\text{max}} \) is the maximum indentation load, \( S_{\text{max}} \) is the stiffness at the maximum load and parameter \( \varepsilon \) is a constant related to the geometry of the indenter.

The above calculation assumed the “sink-in” phenomena of the indented material under the impression. The assumption is invalid for a polymer coating on a stiff substrate in general. Besides, an indenter is never a perfect shape and the tip is rounded at the front due to the fabrication.

The indentation contact area is usually calibrated with standard quartz and it is given as a function of the indentation depth (Oliver and Pharr 1992):

\[
A = C_0 \delta_c^2 + \sum_n C_n \delta_c^{1/2n}
\]

3.29

Where, the parameter \( C_0 \) is related to the geometry of the indenter, \( C_n \) are the deviations from an ideal indenter and the tip rounding effect. The value \( C_0 \) is 24.5 for a perfect sharp Berkovich or Vickers indenter and 5.956 for a cubic corner indenter. Following the procedure and instructions from the technical support from Hysitron, the area function of the cubic corner with tip radius of 40 nm was calibrated as Equation 3.30 obtained from Figure 3.11. Using the calibrated cubic corner tip area function as Eq. 3.30 to calculate another day’s test on the standard sample Quartz again, the calculated results were consistent with the data provided by Hysitron: \( E_r = 69.7 \) GPa and \( H=9.8 \) GPa. The detailed calibration procedure is attached as in Appendix B2.

\[
A = 2.598\delta^2 + 2199.8\delta - 1.0054E5 \delta^{3/2} + 1.0035E6 \delta^{3/4} - 2.464E6 \delta^{1/8} + 1.564E6 \delta^{1/16}
\]

3.30
Figure 3-11  The cubic corner tip area function was calibrated with Quartz
Figure 3-12 Using the calibrated tip area function to calculate another day’s tests with the standard sample Quartz
3.5 Principle and applications of nanoscratching test

3.5.1 Introduction

The scratch test is another major method to characterize the surface mechanics of a material (Tsui, Pharr et al. 1995; Charitidis, Logothetidis et al. 1999; Beake and Leggett 2001; Briscoe and Sinha 2003; Berasategui, Bull et al. 2004; Bruno, Cicala et al. 2004; Wirasate and Boerio 2005). The surface scratching resistance and adhesion strength can be determined, e.g. for multilayered automotive coatings (Chu, Rumao et al. 1998; Lin, Blackman et al. 2001).

The procedure has three stages: 1) AFM scanning the original surface, 2) conducting the scratching test and 3) AFM scanning the post-scratched surface. In the second stage, a scratching indenter with known geometry is forced into a smooth surface and then translated in an x-y plane parallel with the surface. The force in the direction vertical to the surface and lateral velocity of the probe are controlled by the instrument, the vertical displacement of the indenter and the lateral force that resists the indenter motion are material responses. The 2D transducer records the loads and displacements in both vertical and lateral directions with time.

There are two types of scratching modes, a constant load scratching mode and a ramp load scratching mode, as schematized in Figure 3.12. In the constant load mode, the probe is displaced a specific distance along the x-direction, a fixed normal force is applied to move the indenter down into the sample, and then the probe is moved through the material at a constant load. At the end of the horizontal movement, the normal force is stopped and the probe is removed from the trough produced by the test. Alternatively, the horizontal motion of the probe can be accompanied by an increasing normal force on the probe (usually a ramp function).

Examples of the troughs and load vs. displacement curves for both testing modes are shown in Figure 3.13. The constant scratching mode is usually applied for the friction measurement at a certain depth, the ramp scratching mode is commonly used for adhesion evaluation. The scratching data presented in this dissertation were conducted with a cubic probe (one face leading in the front) at the conditions of advancing 10 μm in 30 seconds for both testing modes.
A scratching process dissipates energy. The total scratching energy $E_{\text{total}}$ applied through the indenter is dissipated into three parts as expressed in Equation 3.31 (Briscoe and Sinha 2003). The first part is the energy $E_N$ that is consumed by the material sustaining the vertical force. The second part is the energy that is applied to overcome the resistance for the indenter moving forward laterally, which could be further divided into the ploughing component $E_p$ for material deformation plastically and elastically in tangent direction and friction component $E_F$. The third part is the energy $E_H$ using to overcome the hysteresis loss in the material, mainly in the form of thermal energy.

$$E_{\text{total}} = E_N + (E_p + E_F) + E_H$$ \hspace{1cm} 3.31

Figure 3.14 shows examples of scratching tests in both constant mode and ramp mode. AFM images of an example of the scratching tests in both constant load and ramp load modes. The material scratched is a 350 nm vacuum deposition ceramic coating on a PMMA lens substrate provided by ODC. The load applied was 500 $\mu$N in the constant load mode test, while the maximum load was 50 $\mu$N for a ramp mode test. The post AFM images of the scratching tests (the ramp mode test at the left and the constant load mode test at the right) are shown in Figure 3.14(a). The cross-section profile of the scratches and the morphology at the bottoms of the troughs were also scanned by AFM as shown in Figure 3.14(b) (the ramp mode test at the left and the constant load mode test at the right).
Figure 3-13  Two types of scratching test depending on the way of the load applied: (a) constant load scratching mode and (b) ramp load scratching mode
Figure 3-14  AFM images of a ceramic coating on an acrylic substrate: (a) post-scan of the scratching tests and (b) cross-section profiles of the troughs. The ramp mode test is shown at the left side and the constant load mode test is at the right side.
3.5.2 Applications

Although scratching tests have been widely applied for decades, the quantitatively characterization of the material properties has proven in difficulty. Scratching hardness is the most popular quantity used and it usually is reported in two forms: scratching normal hardness $H_N$ and tangent hardness $H_T$ (Briscoe and Sinha 2003).

$$H_N = q \frac{AF}{\pi d^2}$$  \hspace{1cm} (3.32)

$$H_T = \frac{F_T}{A_T}$$  \hspace{1cm} (3.33)

In which, $q$ is a parameter that the value is between 1 for a purely elastic contact and 2 for a purely plastic contact (Briscoe and Sinha 2003), $d$ is the residual width of the scratching trough, $F$ is the vertical load applied, $F_T$ is the tangential load resisting the indenter moving in the tangential direction, and $A_T$ is the projected contact area between the material and the indenter in the direction of scratching. Since many materials are deformed both elastically and plastically, it is difficult to obtain the accurate contact areas both in vertical and in lateral directions. The possible fractures during the scratching make the measurements even more difficult. Therefore, the scratching hardness coefficients are difficult to measure accurately. Figure 3.14 is an example of a scratched polymer surface; it is obviously difficult to measure the projected contact area in the lateral direction, especially for a nanoscratching test. The sample was a pure acrylic plastic substrate and was scratched in the ramp mode at 100, 200 and 300 µN.

The scratching normal hardness is often referred as dynamic hardness, in contrast to the conventional (static) normal hardness under indentation. Dynamic hardness is quite dependant on the testing conditions such as load function applied, scratching indenter moving speed and the temperature changes. The ratio of the dynamic hardness to the normal hardness is in a range of 0.58 to 1.7 for ductile materials (Briscoe, Evans et al. 1996; Williams 1996).
Figure 3-15  Difficult to accurately measure the contact area at the bottom and the projected area perpendicular to the scratching direction
Another scratching parameter is the apparent friction coefficient $\mu$, which is defined as

$$\mu = \frac{F_r}{F}$$

As discussed in Equation 3.30, the lateral force $F_r$ overcomes both the friction resistance (elastic response) and material plastic deformation in the scratching direction. Usually, the apparent friction coefficient is taken as the intrinsic friction coefficient of a material surface, when a very small vertical load is applied so that the indenter is essentially scratching at the material surface. Figure 3.15 is an example for the intrinsic friction coefficient of about 0.2 measured for a ceramic coating. The material scratched is a 350 nm vacuum deposition ceramic coating on a PMMA lens substrate provided by ODC. The test was conducted using a constant load mode at a constant vertical load of 2 $\mu$N.
Figure 3-16  The intrinsic friction coefficient of a ceramic coating measured by a scratching test at a constant vertical load of 2 μN
Scratching tests are very useful for fracture studies (Lin, Blackman et al. 2000; Huang, Xu et al. 2001; den Toonder, Malzbender et al. 2002; Malzbender and de With 2002; Jardret and Morel 2003; Berasategui, Bull et al. 2004; Jardret and Rynitz 2005; Solletti, Parlinska-Wojtan et al. 2005). The fracture toughness of materials under scratching tests can be similarly calculated as that under the normal indentation tests (Williams 1996). The initial lateral force at which fracture initiates is commonly used to evaluate the material resistance, which can be easily detected from the plots of the lateral force, the penetration depth and the apparent friction coefficient (as defined in Eq.3.34). Figure 3.17 and Figure 3.18 are example scratching tests for (1) a brittle 330 nm ceramic coating and (2) a 300 nm polymer nanocomposite coating respectively, both on the same type of plastic substrates. A ramp testing mode was used and the scratching distance was 10 \( \mu \)N in 30 seconds. The initial fracture events are well defined from both the figures but they behave differently. From Figure 3.17, the initial fracture event of the ceramic coating occurs at the applied vertical load of 120 \( \mu \)N, lateral load at 206 \( \mu \)N and at the penetration depth of 365 nm. The apparent friction coefficient increases discontinuously to a relative constant value of 0.6. From the lateral force profile and the apparent friction coefficient profile, a typical brittle type of fractures occurs after the initial fracture starts. In Figure 3.18, the fracture events of the nanocomposite coating are isolated at the lateral force of 115 \( \mu \)N and 179 \( \mu \)N respectively at the testing conditions. This phenomenon is a typical plastic and ductile fracture when the tensile stress is over the yield point. These different phenomena of the fractures reflect the different fracture mechanisms of materials which will be discussed in Chapter Seven.
Figure 3-17  A ramp nanoscratching test with a ceramic coating on a plastic substrate
Figure 3-18  A ramp nanoscratching test with a nanocomposite coating on a plastic substrate (a) normal and lateral forces, depth and displacement vs. time, and (b) friction coefficient vs. time
3.5.3 Calibration

Similar as the calibration for nanoindentation test, the scratching probe needs to be calibrated for tip area function and transducer in the vertical Z direction; in addition, the transducer needs to be calibrated in the lateral X direction for a 2D transducer. The detailed calibration procedures are attached in Appendix B3b.

3.6 Summary

Indentation and scratching techniques are very powerful tools to evaluate the mechanical properties of materials and the adhesion strength for coatings, especially when the coating thickness is in micro-/nano-scale. The mechanical properties that can be studied by a nanoindentation test are elastic modulus, hardness, residual stress, creep, fracture toughness and interfacial adhesion strength.

Although the nanoindentation testing method has been widely applied for a century, the methodologies of the tests need to be further established in order to be applicable for various materials and in different structures. One of them is how to accurately estimate the indentation contact area, by considering the nature of the material and the substrate effect. The profile of the indented material could be either in “sink-in” or “pile-up” fashion, depending on the nature of the material and the substrate. Another is how to interpret the substrate effect, especially when the substrate is compliant in a layered structure. A general model to address the substrate effect does not exist yet. From the discussion of the selected models (empirical, analytical and numerical) from literature, it is hard to combine the properties of the coating and the substrate, the size effect, residual stress, indenter geometry and testing conditions in one developed model. This could be the reason that limits the application of any of the existing models in general.

For a polymer indentation, a holding step is required in order to eliminate the viscoelastic effect of the material. The holding time is dependant on the specific materials and testing conditions.

There are two types of scratching testing methods: a constant load mode and a ramp load mode. Nanoscratching test is the most popular way to characterize the adhesion properties of a layered structure. The critical load when the fracture initiates is
a well defined quantity so that it is commonly used to evaluate the adhesion strength. Other properties can also be studied, such as the apparent friction coefficient, the scratching tangent hardness $H_T$ and the scratching normal hardness $H_N$ (dynamic hardness in contrast to the conventional indentation hardness). However, since many materials are deformed both elastically and plastically, it is difficult to obtain the accurate contact areas both in vertical and in lateral directions. The possible fractures during the scratching make the measurements even more difficult. Therefore, the scratching hardness is difficult to be measured accurately.

In order to have a repeatable and accurate measurement of the mechanical properties, the nanoindentation and nanoscratching instruments need to be carefully calibrated. Besides, it is critical to calibrate the indenter tip area function.
Chapter Four : Nanoindentation behavior of ultrathin polymeric films on stiff substrates

(This chapter is based on the following reference: Polymer, Volume 46, Issue 25, 28 November 2005, Pages 11768-11772.)

4.1 Introduction

Ultrathin films of polymeric materials have a number of applications, including scratch-resisting coatings, protective barriers, optical filters, and layered constructions. For example a scratch-resistant lens coating can improve the longevity of plastic eyeglass lenses, and multilayered nanoscaled coatings with unique optical properties can be constructed to improve optical performance. In other applications, semi-permeable ultrathin layers can be used to protect surfaces from water or oxygen. In each of the applications, the physical properties of ultrathin layers, individually or in layered constructions, are difficult to determine by conventional methods such as tensile and compression tests. Similar difficulties exist in measuring the mechanical properties of quasi-one dimensional nanoscale materials such as nanotubes (Falvo, Clary et al. 1998; Pan, Xie et al. 1999; Wang 2004) nanobelts for micro-optoelectronic and biomedical applications (Wang 2004) (Mao, Zhao et al. 2003; Yang, Jiang et al. 2005) and nanofilms (Carneiro, Teixeira et al. 2004; Richert, Engler et al. 2004). As more applications are developed for submicron polymeric structures, there will be a greater need for direct measurements of physical properties as materials have been applied, fabricated or polymerized in place.

Studies of ultrathin polymeric films suggest that unusual properties, for example, the lower glassy-rubbery transition temperature (Tg) at near surfaces (Jones and Richards 1999), are often the result of the large volume fraction of interfacial regions (Teichroeb and Forrest 2003) that constitute significant portions of the material at ultrathin scales. Measurement of mechanical properties on and near polymer surfaces is likely to provide improved understanding of these unique behaviors and to improved control of the fabrication and polymerization processes of multilayer materials. In principle, there are two basic approaches in assessing viscoelastic properties of
polymer surfaces; a) contact mechanics (Ge, Pu et al. 2000; Fischer 2002) and b) surface relaxation (Hamdorf and Johannsmann 2000; Hutcheson and McKenna 2005). However, most measurements reported in literature were done on thin polymeric films with thickness more than several microns (Beake and Leggett 2001; Li, Palacio et al. 2002) (Nowicki, Richter et al. 2003). There are few studies of the mechanical properties of nanoscaled polymeric films that include the effects of substrates, and the effects of multilayered films. In this work, a nanoindentation study was conducted on the ultrathin polymeric coatings, at the thickness of 47 nm, 125 nm and 3000 nm, on the stiff silicon wafer substrates. The modulus of a polymer material is usually less than 10 GPa, while the modulus of a silicon wafer is 176 GPa. Therefore, these layered samples can be taken as a typical a compliant coating on a stiff substrate system for the study of the substrate effect on the elastic response and for the study of the flow behavior of a submicron polymeric material.

4.2 Sample preparation

4.2.1 Materials

The polymer coatings were made by spin-coating from polymer precursor solution. The solution consisted of dipentaerythritol pentaacrylate from Sartomer SR399 (CAS# 60506-81-2) and 5wt% photoinitiator 1-hydroxy cyclohexyl phenyl ketone (Ciba-Geigy 184, CAS# 947-19-3), that were dissolved in equal weights of acetone and isopropanol co-solvents. The free radical reaction was initiated by dissociation of the photoinitiator molecules under UV radiation, leading to the formation of densely cross-linked polymers exhibiting good mechanical strength, thermal stability and resistance to solvent absorption ideally suited as surface protective coatings and dental restorative materials (Anseth 1996). The high crosslinking level of cured SR399 leads to strong, high modulus acrylates. The molecular structure of the SR399 monomer was previously shown in Figure 2.4 in Chapter Two.

4.2.2 Procedure

The nanoscaled polymeric films were spin-coated on silicon wafers at 1,000 rpm using a Spin Coater (Optical Dynamic Corporation, Louisville, KY). The thickness and
surface quality of the ultrathin polymeric thin films were controlled by the solute concentration and spin speed (Meyerhofer 1978).

All of the films were cured for 90 seconds in the presence of CO\(_2\) under UV light from a germicidal lamp having an intensity of 4mW/cm\(^2\) at 5 cm distance. The polymerization degree or [C=C] conversion rate was monitored by Fourier Transform Infrared Spectroscopy (FTIR) at 64 scans and resolution 4 cm\(^{-1}\) with Mattson Galaxy Series 3000 (Madison, WI).

4.2.3 Sample characterization

4.2.3.1 Degree of polymerization

The FTIR spectra of the polymeric films before and after curing are depicted in Figure 4.1. For comparison, the peaks at 809 cm\(^{-1}\) have been normalized in scale to the peak of ketone at 1726cm\(^{-1}\). The extent of the reduced IR absorption of the acrylic double bond [C=C] at 809 cm\(^{-1}\) was related to the amount of polymerization (Decker and Jenkins 1985). The polymerization degree of this type of high functional monomer (Studer, Decker et al. 2003) was measured to be 76%, 83% and 82% for the films of 47 nm, 125 nm and 3000 nm films, respectively, which suggests that the three films were chemically similar. These degrees of conversion are well above that of the gel point (~20%), so they all should have solid-like elasticity.
Figure 4-1  The FTIR spectra of the SR399 films of (A) before curing and after curing, (B) 47 nm, (C) 125 nm and (D) 3000 nm

(All spectra were normalized to the peak of ketone at 1726 cm$^{-1}$. The absorbance of acrylic double bond at 809 cm$^{-1}$.)
4.2.3.2 Surface roughness

The surface roughness of the polymeric films was determined using the tapping mode on Digital Instruments MMAFM-2 (Woodbury, NY) as shown in Figure 4.2. The deviation of surface height from the mean plane, \( R_a \) (the arithmetic average of the absolute values), were 0.281 nm, 0.233 nm and 0.250 nm for thin films of 47 nm, 125 nm and 3000 nm, respectively. A typical topography of the 47 nm film is shown in Figure 4.3. In general, the minimum indentation depth should be 20 times of \( R_a \) in order to restrict the uncertainty in contact area between the tip and the film to within 5 percent error (Fischer-Cripps 2002). Thus the minimum indentation depth required to eliminate the effect of surface roughness is about 5nm. The smallest indentation depth in all the indentation tests was then controlled at about 5 nm.

4.2.3.3 The thickness of the coatings

The thicknesses of the spin-coated polymer thin films were measured by a profilometer from Ambios Technology XP-1 (Santa Cruz, CA).
Figure 4-2  AFM images of the surface of the 47 nm film
4.2.3.4 The elastic modulus measurement

The elastic modulus of the coatings were measured by nanoindentation. The nanoindentation tests are performed in a Hysitron TriboScope (Minneapolis, MN) attached to a Quesant (Agoura Hills, CA) atomic force microscope (AFM). A diamond NorthStar cubic indenter with a nominal tip radius of 40 nm (Minneapolis, MN) is used. The penetration depth and applied load are used to compute the modulus of the films.

The nanoindentation tests were carried out using the load control mode with the indentation load in the range of 0.8 to 100 μN. The loading rate and unloading rate were in the range of 0.16 to 20 μN/s. To eliminate the effect of viscoelastic deformation on the measurement of the nominal reduced contact modulus, the methodology “held-at-peak-load” (Briscoe, Fiori et al. 1998; Ngan and Tang 2002) was used. The results were averaged over more than 5 indentations for each testing conditions. Using the Oliver and Pharr theory (Oliver and Pharr 1992), the reduced contact modulus, \( E_r \), was calculated from the upper portion of the unloading curve as

\[
E_r = \frac{\sqrt{\pi} \frac{dF}{d\delta}}{2\sqrt{A}}
\]

4.1

Here, \( A \) is the contact area between the film and the indenter, \( F \) is the peak indentation load, \( \delta \) is the indentation depth, and \( \frac{dF}{d\delta} \) is the tangent to the upper portion of the unloading curve. No sink-in or pile-up effect was taken into account in the calculation.

4.3 Elastic modulus measurement results

4.3.1 The 10% rule of thumb

Figure 4.3 shows the dependence of the reduced contact modulus on the relative indentation depth for the indentations on all three films with a holding time of 2 seconds. From these we see that the polymeric film of 3000 nm behaves as a bulk material relative to the films of 47 nm and 125 nm, and the reduced contact modulus of the 3000 nm film, 4.86 ± 0.32 GPa, is independent of the indentation load. For the indentation load less than or equal to 1 μN, the reduced contact modulus are 5.62 ± 1.52 GPa and
4.78 ± 1.60GPa for the 47 nm and 125 nm films, respectively, compatible to that of the 3000 nm film. No scaling effect is observed on the behavior of surface elasticity for these ultrathin polymeric films. The measured mechanical property is consistent with the degree of polymerization monitored by the FTIR.
Figure 4-3  Dependence of the reduced contact modulus on the relative indentation depth
4.3.2 The substrate effect

Figure 4.4 shows the dependence of the reduced contact modulus on the indentation depth ($\delta$) for indentations on all three films with a holding time of 2 seconds. The reduced contact moduli for both the 47 nm and 125 nm films start to increase with the increase of the indentation depth when the indentation depth is more than 10% of the film thickness. This is due to the effect of the substrate. For the nanoscaled polymeric films deposited on silicon wafers, the Young’s modulus of silicon wafers is 176 GPa (Barsoum 1997) about 37 times more than the Young’s moduli of the films. Thus, the silicon substrate can be treated as a rigid substrate as compared to the polymeric films. These results support the published suggestion for indentation tests (Fischer-Cripps 2002) – that the effect of substrate on the reduced contact modulus is negligible when the indentation depth is less than 10 percent of the film thickness. In such that the reduced contact modulus is constant for an indentation depth less than 10% of the film thickness.

For the reduced contact moduli at the indentation depth over 10% of the film thickness when the substrate effect starts, we can fit the experiment data using the analytical model (Yang 2003). This model reveals that the load-displacement relationship and contact stiffness are different for a coating on a rigid substrate from an impressible elastic half space under the assumptions of an incompressible elastic thin film and a frictionless contact between the spherical or conical indenter and the material. In order to apply this model, we approximate the cubic indenter as a conical indenter with a half included angle of 42.28° (to have the same depth to area as the cubic indenter), and assume that the polymeric films are incompressible and the contacts over the interface between the indenter and the film and that between the film and substrate are non-slip. Considering the corrected factor of 4 for non-slip contact over both the contact interfaces for the indentation of thin films using the flat-ended indenter (Yang 1998) and using the indentation load-depth relationship for the indentation of incompressible thin films with frictionless contact between the indenter and the film and the non-slip contact between the film and the substrate (Yang 2003), we obtain
\[
F = \frac{\pi \mu \delta^2 \tan^4 \theta \left( \frac{3}{2} \right)^5}{5h^3}
\]

4.2

Assuming that Eq. 4.1 can be applied to the indentation of thin films and using the relation \( a = 3\delta \tan \theta / 2 \) for the indentation of thin films (Yang 2003), one can calculate the nominal reduced contact modulus, \( E_r \), as

\[
E_r = \frac{15}{4} \frac{F^{3/5}}{\tan \theta} \left( \frac{\pi \mu \tan^4 \theta}{5h^3} \right)^{2/5}
\]

4.3

where \( a \) is the contact radius, \( \theta \) the half included angle, and \( \mu \) the shear modulus of the film. Assuming that the polymer is incompressible, \( v_s \) is 0.5 [acrylic Poisson ratio is about 0.4]. For the diamond tip, \( E_i \) is 1141 GPa and \( v_i \) is 0.07. Using the reduced contact modulus for \( F \leq 1 \mu N \) and the following equations,

\[
\frac{1}{E_r} = \frac{1-v_s^2}{E_s} + \frac{1-v_i^2}{E_i}
\]

4.4

\[
\mu = \frac{E_s}{2(1+v_s)}
\]

4.5

Thus, \( \mu = 1.22 \) GPa. Here \( E_s \) and \( E_i \) are the modulus of the film and the modulus of the tip respectively, and \( v_s \) and \( v_i \) are the Poisson ratios of the film and the tip respectively.

Using \( \mu = 1.22 \) GPa, the normal reduced contact modulus as calculated from Eq. 4.3 for larger indentation loads is also depicted in Figure 4.4. Obviously, Eq. 4.3 gives the same trend as observed in the tests, while the calculated contact modulus is about two times less than the experimental results. This is due to the use of the contact radius, \( a = 3\delta \tan \theta / 2 \), in the derivation of Eq. 4.3. It is known that Eq. 4.1 is only valid for the indentation of an elastic half-space. Thus, the experimental data overestimate the nominal reduced contact modulus for the indentation of thin films at the indentation depth over 10% of the film thickness. To consider the effect of contact area on the experimental data, one needs to use the relation between the contact radius and the indentation depth, \( a = 2\delta \tan \theta / \pi \), for the indentation of an elastic half-space by a conical indenter [29]. Using the same procedure in deriving Eq. 4.3, one obtains
\[ \tilde{E}_r = \frac{3\pi}{4} E_r = \frac{45\pi}{16} \frac{F^{3/5}}{\tan \theta} \left( \frac{\pi \mu \tan^4 \theta}{5h^3} \right)^{2/5} \]

in which \( \tilde{E}_r \) is the normal reduced contact modulus using the contact area for the indentation of an elastic half-space by a conical indenter. For comparison, \( \tilde{E}_r \) is also plotted in Figure 4.4. Obviously, the experimental results support Eq. 4.6.

Obviously, the classic model estimated the reduced modulus about 1.5 times higher than the modified model with a more accurate indentation contact radius. In fact, the profile of the indented material is typically “piled-up” near the upper contact surface between the indenter and the soft film (\( \delta_c > \delta \)). This material response is typical for a compliant coating (polymer) on a stiff substrate (silicon wafer) as shown in Figure 4.5. The cartoon of Fig. 4.5 mimics the real “pile-up’ profile shown in Figure 3.5.
Figure 4-4 Dependence of the reduced contact modulus on the indentation load
Figure 4-5  The "pile-up" profile of the indented material common for a polymer coating on a stiff substrate
4.4 Viscoelastic behavior at the surface of polymeric coatings

4.4.1 Holding time of nanoindentation

In general, the deformation behavior of polymers is viscoelastic. During constant indentation loads, viscous flow of the polymer is anticipated and may affect the data if it is still occurring as the unloading process begins. This potential problem was evaluated by performing experiments with different holding times. Figure 4.6 shows the dependence of the reduced contact modulus on the holding time for indentations of the 125 nm film with a maximum indentation load of 1 μN. The reduced contact modulus obtained from the unloading curves, according to the Oliver-Pharr's model, decreases with the holding time and converges to a relatively constant value of 4.78 GPa for holding times greater than 2 seconds. This effect is interpreted as an elastic rebound when the indenter load is removed before a quasi steady-state polymer flow is achieved. It is similar to the “bulge” phenomenon observed in the indentation tests without holding time at lower unloading rates (Ngan and Tang 2002) and verified by numerical simulation (Cheng and Cheng 2005). The time for viscoelastic polymer material to reach a quasi steady-state flow under a constant load can be determined from the contact stiffness $\frac{dF}{d\delta}$, the slope of the initial unloading curve, which changes with the holding time as in Figure 4.7. The slope is very steep without a holding time, then decreases sharply with holding 1 second, and becomes almost constant after holding 2 seconds. From the Oliver and Pharr’s model (Eq. 3.4), the value of the contact stiffness directly determines the calculated elastic modulus.

Errors in the measurement of the reduced contact modulus due to the dynamic rebound effect due to the inertial force at the moment of unloading, the indenter needs to be held at the constant indentation load for a certain amount of time in order to eliminate the dynamic rebound effect and to reach the quasi-steady flow state. It should be pointed out that the holding time to reach the quasi-steady flow state is a function of the loading rate and the mechanical properties of materials. For small loading rates, the inertial force is small, and it requires less holding time for the indentation motion to attain the quasi-steady flow state. Similarly, stiffer films require less holding time.
4.4.2 Surface flow behavior of the polymeric coatings

Figure 4.7 shows the time dependence of the indentation depth for the indentations on the polymeric film of 125 nm at a constant indentation load of 1 μN. The indentation depth between the end of the loading phase and the start of the unloading phase is a linear function of the holding time, which is different from the relation for Newtonian fluids (Yang and Li 1997). The indentation velocity is independent of the indentation stress even though the indentation stress decreases with the increase of the indentation depth. It is expected that the flow behavior of the thin films is shear-thinning.

Under the quasi-steady flow state, the effect of elastic deformation on the flow behavior is negligible. The flow behavior of the polymeric films can be described as

\[ \tau = k\dot{\gamma}^n \]  

for \( n = 1 \), \( k \) is a constant (for \( n = 1 \), \( k \) is the viscosity). Approximating the cubic indenter as a conic indenter and using the results given by Hill (Hill 1992) from the similarity analysis, one obtains

\[ \int_0^t F^n dt = \alpha \delta^{2n} (\cot \theta)^{2n-1} \]  

which reduces to the result for Newtonian fluids (Yang and Li 1997). Here \( \alpha \) is a constant depending on \( k \) and \( n \). Under a constant indentation load, Eq. 4.8 gives the time dependence of the indentation depth as

\[ F^n \Delta t = \alpha (\cot \theta)^{2n-1} (\delta^{2n} - \delta_0^{2n}) \]  

Here \( \delta_0 \) is the indentation depth before applying a constant indentation load to the indenter. When \( F \) is constant, the change in time should be directly proportional to the difference, \( \delta^{2n} - \delta_0^{2n} \). Since the relation between time and indentation depth is linear as shown in Figure 4.7, one obtains \( n = 1/2 \). Thus, the near-surface flow behavior of the ultrathin polymeric films is shear-thinning.
Figure 4-6 Effect of the holding time on the reduced contact modulus for the indentations on the polymeric film of 125 nm with the maximum indentation load of 1 μN
Figure 4-7  The contact stiffness vs. the holding time
Figure 4-8  Time dependence of the indentation depth for the polymeric film of 125 nm at an indentation load of 1 μN
4.5 Summary

The deformation behavior of the ultrathin polymer coatings on higher modulus substrates has been evaluated using the nanoin dentation technique. The reduced contact modulus increases with the indentation load due to the effect of substrate. The effect of substrate on the reduced contact modulus can be described by an elastic contact model of the indentations that has a larger contact radius than the film thickness. Quantitative agreement between the model and the experimental results is obtained. No scaling effect was observed on the behavior of surface elasticity for ultrathin polymeric films. The viscoelastic deformation of the films has a significant effect on the measurement of the reduced contact modulus unless the unloading curve is begun after the indenter's motion has reached a quasi steady-state. It is found that there exists a critical holding time where, for times exceeding a critical holding time, the dynamic effect is negligible. The flow behavior of the SR399 ultrathin films subjected to constant indentation loading displays shear-thinning characteristics and can be described by a linear relation between the indentation depth and time with the stress exponent being 1/2.
Chapter Five: Elastic response of stiff ultrathin polymeric coatings on compliant substrates: modeling

5.1 Introduction

Layered structures are being developed to meet various applications, for example, functional multi-layers in magnetic storage systems, semiconductor chips, and capacitors (Bull and Korsunsky 1999; Hsueh and Ferber 2002; Hsueh 2003). Some of these layered structures are hard protective topcoats that are applied in advanced products such as diamond-like carbon coatings on aluminum substrate for the magnetic hard disk industry and anti-scratch layers on optical lens substrates (Tsui, Pharr et al. 1995; McGurk and Page 1997; Tsui, Vlassak et al. 1999; Charitidis, Gioti et al. 2004). These topcoats are usually mechanically stronger and tougher than the underneath layers to improve the product lifespan and make the product more reliable. Measurement of the in situ mechanical properties of these topcoats is very critical. Since the thickness of the protective coats usually ranges from micrometers down to nanometers, conventional mechanical testing methods such as tensile tests, bending tests and impact tests are not applicable. Nanoindentation can directly measure the mechanical properties of these coatings.

The classic theory of elastic modulus of bulk monolithic materials characterized by nanoindentation has been thoroughly studied (Oliver and Pharr 1992; Cheng, Cheng et al. 1998; Malzbender, den Toonder et al. 2002) and discussed in Chapter Three (Oliver and Pharr 1992),

$$E_r = \frac{\sqrt{\pi}}{2\sqrt{A}} \frac{dF}{d\delta}$$

Equation 3.3 is not applicable for thin coating-substrate systems since the material responses unavoidably combine deformations from both the coat and the substrate, and the indentation contact radius is different from that in a bulk material.
system as discussed in Chapter Four. The extent of the influence from the substrate or the critical indentation depth that substrate effect appears depends on the elastic modulus and the hardness of both coating and substrate, coating thickness, applied load, indentation depth, the geometry of the indenter (Malzbender, den Toonder et al. 2002; Xu and Rowcliffe 2004), coating cracking (Hsueh 2001; Beegan, Chowdhury et al. 2004), residual stress (Kraft and Nix 1998; Brennan, Munkholm et al. 2000; Swadener, Taljat et al. 2001; Hsueh 2002; Malzbender and Steinbrech 2003; Lepienski, Pharr et al. 2004; Malzbender 2004; Yang 2004) and interfacial properties (Bull and Rickerby 1990; Wu, Moshref et al. 1990; Berasategui, Bull et al. 2004) ..

The simple way to neglect the substrate effect for directly measuring the property of coatings is to control the indentation depth to less than one tenth of the coating thickness. This rule-of-thumb has been proven valid for an ultrathin polymeric coating with thickness less than 100 nm on a much stiffer silicon wafer substrate by using a nanoindentation with a sharper indenter as discussed in Chapter Four (Geng, Yang et al. 2005). This rule-of-thumb may not be applicable for hard and stiff coatings on soft and compliant substrates since their plastic deformation occurs at much lower load or indentation depth (Tsui, Vlassak et al. 1999; Saha and Nix 2002; Beegan, Chowdhury et al. 2004).

Due to the difficulties for both the unknown pressure over the contact area at the indenter-coating interface and the boundary conditions at the coating-substrate (Hsueh and Miranda 2004), a general closed form solution is not easy to be developed. Many empirical and analytical models have been developed for the case of a compliant coating on a stiff substrate to extract the intrinsic property of the coating from the substrate influences (Doerner, Gardner et al. 1986; Korsunsky, McGurk et al. 1998; Saha and Nix 2002; Tsui, Ross et al. 2003; Hsueh and Miranda 2004). The attempts to solve the case of a stiff coating on a compliant substrate have not been as successful as for the case of a compliant coating on a stiff substrate yet (King 1987; Gao, Chiu et al. 1992; Tsui, Vlassak et al. 1999; Kramer, Volinsky et al. 2001; Beegan, Chowdhury et al. 2004; Berasategui, Bull et al. 2004; Ni and Cheng 2005). Many models to separate the elastic modulus of the stiff coating from the compliant substrate are only applicable for specific coating-substrate systems, for example, when the coating and the substrate are
nearly plastically homogeneous, the “intrinsic” coating modulus can be extracted from
the substrate influence by using the material “characteristic parameter,” the ratio of load
to the square of unloading stiffness \( \left( \frac{F}{S^2} \right) \) (Joslin and Oliver 1990; Saha and Nix 2002).
Usually other factors have not been able to be considered when developing a general
solution for stiff coatings on compliant substrates, such as the interfacial adhesion
strength (Wu, Moshref et al. 1990; Tsui, Ross et al. 1997), residual stress (Ghaffari,
Wang et al. 1996; Hsueh 2003) and fracture of the coatings (debonding or cracking)
(McGurk and Page 1997; Korsunsky, McGurk et al. 1998; Beegan, Chowdhury et al.
2004). There are no existing models in literatures specifically developed for an ultrathin
polymeric coating on a more compliant substrate.

The aim of this work is to compare the validity of several models for modeling
data for a single-layered stiffer nanoscale densely cross-linked polymeric coating on a
more compliant acrylic substrate. The elastic modulus of the coatings is about as twice
as that of the substrate. In this study, the coatings were spin-coated individually on soft
plastic substrates at the thicknesses of 47 nm, 125 nm, 220 nm and 3,000 nm
respectively.

5.2 Experiment preparation

Four polymeric coatings of dipentaerythritol pentaacrylate from Sartomer SR399
at the thickness of 47 nm, 125 nm, 220 nm and 3000 nm were individually spin-coated
and UV cured on acrylic optical lens substrates provided by Optical Dynamics (Louisville,
KY). The sample preparation and characterization methods are the same as previously
reported (Geng, Yang et al. 2005). To simplify for the modeling study, no sink-in or pile-
up effect was taken into account in the calculations. The “intrinsic” reduced modulus of
SR399 coatings was measured for the 3,000 nm coating at indentation depths less than
one-tenth of the coating thickness on a rigid silicon wafer substrate (Geng, Yang et al.
2005). The mean intrinsic modulus was 6.08 ± 0.17 GPa. The compliant optical lens
substrate is about 3 mm thick and was treated as a bulk monolithic material. The
reduced modulus was measured directly by using the Oliver and Pharr model (Oliver
and Pharr 1992) for bulk monolithic materials and gave values of 2.95 ± 0.08 GPa. The
coating is a factor of two stiffer than the substrate.
The nanoindentation tests were conducted with the nanoindentation instrument from Hysitron, the testing conditions and the indenter used as in previous work (Geng, Yang et al. 2005). The radius of the normal cubic indenter tip was verified again by AFM images of the impression of the indentations in the standard sample of fused quartz from Hysitron (Figure 1). The radius is about 40nm which is consistent with the nominal radius provided by the manufacturer.

For calculation purposes, the cubic geometry can be converted to an equivalent conical indenter by the same equal projection principle, that is, the same contact area at the same indentation depth (Gao, Chiu et al. 1992). Then, the contact radius of the indenter with the indented material is calculated as

$$a = \sqrt{\frac{A}{\pi}}$$  \hspace{1cm} (5.1)

Where $A$ is the contact area between the surface of the indented material and the indenter. For viscoelastic polymers, the creep effect needs to be corrected and the contact depth in this study was determined by

$$\delta_c = (\delta_{max} - \delta_{creep}) - 0.75 \times F_{max} / S$$  \hspace{1cm} (5.2)

Where, $\delta_{max}$ is the maximum depth, $\delta_{creep}$ is the depth shift during the holding time of the 2 seconds which was determined in the previous studies (Geng, Yang et al. 2005), $F_{max}$ is the maximum load, $S$ is the stiffness or the tangent to the upper portion of the unloading curves ($\frac{dF}{d\delta}$). The coefficient of 0.75 is a numerical result for a cubic corner indenter, the same as a Berkovich indenter [The technical support of Hysitron].
Figure 5-1  AFM image of an imprint (top) and its cross-section profile (bottom) indented by a cubic corner indenter into a fused Quartz
5.3 Experiment results

5.3.1 Compliant substrate effect

The data of the effective moduli of the coatings at the thickness of 47nm, 125nm, 220nm and 3,000nm on the compliant substrates respectively are shown in Figure 2. For comparison, the modulus of the pure compliant substrates at the thickness of 3 mm and the modulus of the coating at the thickness of 3,000nm on a rigid silicon wafer substrate are also presented in Figure 5.2.

The mean modulus of the 3 \( \mu \text{m} \) coating on a silicon wafer at low indentation depth is taken as the property of the bulk coating material. From Figure 5.2, the mean modulus of SR399 bulk coating material and the modulus of the pure compliant lens substrate are measured as 6.08 ± 0.17 GPa and 2.95 ± 0.08 GPa respectively. All the coatings including the one with the thickness of 3 \( \mu \text{m} \) on the compliant substrates show lower moduli than that of the bulk coating material itself even at the very low load of 2 \( \mu \text{N} \). This indicates that the substrate effect comes into play at a very low load or at a very shallow indentation depth. All the coatings on compliant substrates have higher moduli at shallow indentation depths and decrease gradually at deeper indentation depths. The influence of the softer compliant substrate on the moduli increases with indentation depths. At similar indentation loads, thinner coatings have lower moduli.
Figure 5-2  The effective moduli of the coatings, and coating/lens and coating/silicone pairs
The compliant substrate effect can be seen even for much thicker coatings. From Figure 5.2, the effective modulus of the 3000 nm coating on the compliant lens substrate is about 15-20% lower than its counterpart on a silicon wafer substrate at the indentation depth less than 300 nm (10% of the coating thickness); above 300 nm, the reduced modulus of the coating/lens laminate decrease rapidly with indentation depths. It seems that the reduction of the effective elastic modulus behaves differently before and after 10% the coating thickness. More understanding is desired to interpret this phenomenon. The compliant substrate effect can also be detected from the contact indentation depth, as shown in Figure 5.3. For example, at very low indentation load of 2 μN, the contact indentation depth of the coating/lens laminate is about 24% higher than the coating/silicon laminate.
Figure 5-3  The contact depths of the lens, the coating/lens laminates, and the coating/silicone laminate at a load of 2 μN
5.3.2 Coating thickness effect

The effective moduli of each coating on the compliant substrate can be plotted as a function of the relative indentation depth (R.I.D.), the ratio of the indentation depth to the coating thickness as in Figure 5.4. Although the effective moduli of the coating-substrate system vary with indentation depth for different thickness coatings, all four coatings have similar values of the effective modulus of about 6.0 GPa when R.I.D. is less than 0.1. Then, the effective moduli start to decrease with increasing indentation depth. For the 3 μm coating, the curve appears to change slope at an R.I.D. of 0.1. The 220 nm coating appears to change slope at an R.I.D. closing to 2.0. The two thinner coatings do not seem to have sharp changes in the moduli vs. R.I.D. curves. The change of slope could be due to the fractures (delamination and/or cracking) of the coatings.

Major fracture events can be detected from the load-displacement curves and the nanoindentation induced ultrathin coating delamination has been investigated (Geng, Yang et al. 2006). It is expected that there will be a sudden increase of the penetration depth and a sudden decrease of the unloading stiffness when a failure (crack and/or delamination) of the coating occurs. Consequently, the modulus drops significantly when a fracture occurs according to the Oliver and Pharr’s equation (Eq. 3.3). The initial delamination occurs at the indentation depth of 520.7±33.5nm (the best estimated), 829.9±13.2nm, 1075.1±55.5nm and 439.8±9.3nm for the coatings of 47 nm, 125 nm, 220 nm and 3 μm, respectively. The respective R.I.D. is 11.09, 6.64, 4.89 and 0.15. Comparing with Figure 5.4, the effective moduli seem to start to drop at a shallower indentation depth than the one that the delamination can be seen from the phenomena of the discontinuities at the indentation load-displacement curves. This could be because that there are some fine failures of the coatings, such as slight cracks or crazes, actually occurring at even earlier stages.

Nevertheless before the failures of the coatings occur, or under the R.I.D of 2 for all submicron coatings tested (47 nm, 125 nm and 220 nm), the effective moduli present a very similar trend as a function of R.I.D., as shown in Figure 5.5.
Figure 5-4  The moduli of the coating/lens laminates vs. the relative indentation depth (R.I.D.)
Figure 5-5  The relationship between $E_r$ and R.I.D. before the coating fractures (Figure 5.4 at R.I.D. $\leq 2.0$)
The effective modulus of the SR399 coating with different thickness on the compliant substrate is plotted as a function of the elastic indentation depth \( \delta_e \) in Figure 6(a). \( \delta_e \) was defined in Figure 3.2. We can see that the effective modulus of 220 nm coatings is close to 3,000 nm coatings and is clearly higher than 47 nm coating at shallow indentation depths; but converges to the modulus of 47 nm at deeper indentation depths. The similar trend is found between the creeping or viscoplastic deformation of the indented material and the applied indentation loads, that is, the substrate effect appears faster for thinner coatings as intuitively expected, shown in Figures 5.6(b). The common feature for both Figure 5.6 (a) and (b) is that the effective mechanical properties and the material deformation transit smoothly between the coatings at the different thickness. Therefore, the coating thickness is an important factor that determines when and to which extent the substrate effect comes into play.
Figure 5-6  (a) The effective moduli vs. elastic indentation depth and (b) creep distance vs. indentation load.
5.4 Modeling

5.4.1 Hsueh and Miranda’s model - at low indentation depths

5.4.1.1 Modeling with a spherical indenter

From Figure 5.1, the cubic indenter tip is more like a sphere at the front of the indenter due to the tip rounding. Therefore, it is expected that the tip’s spherical geometry will control the indentation behavior at the low indentation depths of about 30 nm for a tip radius of approximately 40 nm.

As discussed in the Section 3.2.2.2 at Chapter Three, for a spherical indenter and at Hertzian indentation conditions (ie. pure elastic contact between the tip and the indented material), Hsueh and Miranda (Hsueh and Miranda 2004; Hsueh and Miranda 2004) proposed the relationship of the overall indentation displacement to the ratio of coating thickness to contact radius and the ratio of coating-to-substrate Young’s modulus ($\frac{E_c}{E_s}$):

$$\delta = \alpha^{-2/3} \left[ \frac{9(1-\nu_c^2)^2 F^2}{16RE_c^2} \right]^{1/3}, \quad 5.3$$

where,

$$\alpha = \left\{ 1 + \frac{E_c(1+\nu_c)}{\pi E_s(1-\nu_c^2)} \left[ (3-2\nu_s)\lambda_1 + \lambda_2 \right] \right\} - \frac{1}{\pi(1-\nu_c)} \left[ (3-2\nu_c)\lambda_1 + \lambda_2 \right]^{-1} \quad 3.9$$

where $F$ is the maximum indentation load, $\nu_c$ is the coating’s Poisson ratio, $E_c$ is the coating modulus, $R$ is the radius of the spherical indenter, $\nu_s$ and $E_s$ are the Poisson ratio and Young’s modulus of the substrate respectively. $\lambda_1$ and $\lambda_2$ are the functions of $t / a$. $a$ is the contact radius between the tip and the surface of the indented material.

$$\lambda_1 = \frac{\pi}{2} \left( 1 + \frac{t^2}{a^2} \right) - \frac{t}{a} - \left( 1 + \frac{t^2}{a^2} \right) \sin^{-1} \left[ \frac{t}{a} \left( 1 + \frac{t^2}{a^2} \right)^{-1/2} \right] \quad 3.10a$$

$$\lambda_2 = -\frac{\pi}{2} \left( 1 + \frac{3t^2}{a^2} \right) + \frac{3t}{a} + \left( 1 + \frac{3t^2}{a^2} \right) \sin^{-1} \left[ \frac{t}{a} \left( 1 + \frac{t^2}{a^2} \right)^{-1/2} \right] \quad 3.10b$$
The method was developed based on the macro-scale coating-substrate systems, it has not been verified for ultrathin coatings yet (Hsueh and Miranda 2004).

5.4.1.2 Modeling results

Assuming the indented materials are impressive, i.e., Poisson ratios of the coating and the substrate are 0.5, and applying the known the intrinsic modulus of the substrate \( E_s = 2.95 \pm 0.08 \ \text{Gpa} \) and varying modulus of the coating around the intrinsic value \( E_c = 6.08 \pm 0.17 \ \text{GPa} \), the effective elastic indentation depths \( \delta \) were calculated by using Hsueh and Miranda’s model (Eq.5.3). Figure 7(a-d) shows the modeling \( \delta \) values comparing with the experimental data presented as solid circles for the four coatings on the compliant substrates respectively.
Indentation load, $\mu N$

Elastic depth, nm

(a)

(b)

Measured

if Ec = 3 GPa

if Ec = 4.5 GPa

if Ec = 6 GPa

if Ec = 12 GPa

if Ec = 24 GPa
Figure 5-7  Comparing the effective elastic indentation depths between the experimental and modeling values for the coatings: (a) 47 nm, (b) 125 nm, (c) 220 nm and (d) 3,000 nm.
From Figure 5.7(a-d), overall speaking, the intrinsic coating elastic modulus of 6 GPa is a relatively good fitting value for all submicron-meter coatings except for the 3 μm coating. These results indicate that the Hsueh and Miranda’s model works well for submicron meter coatings at very shallow indentation depths, that is, as long as the indenter tip penetrated in the coatings remains as a spherical geometry. As seen in Figure 5.1, this cubic indenter should have a spherical front of the tip when the indentation depth is less than 30nm. This can also be proven by the fact that the fitting quality is better at a lower indentation depth when the front tip of indenter is in a more perfect “spherical” shape. For the 3 μm coating, since the calculated values of α were negative and thus $\alpha^{-2/3}$ had no real numerical resolution when varying $E_c$ at the shallow indentation depths; thus, Eq. 5.3 is not applicable to predict the effective elastic indentation depth in this case. The reason could be that the radius of the “spherical” indenter used is so small for 3 μm thick coating that the tip could not “feel” a strong substrate effect at a very low indentation depth.

Generally speaking, the indented material behaves more elastically at the condition that the radius of a spherical indenter $R$ is much larger than the contact radius $a$ between the indenter and the material. For example, it is common to use a flat indenter to study the pure elastic indentation response. Considering the Hsueh and Miranda’s model was developed based on the assumption of a pure elastic response (Hertzian indentation condition), it is predictable that the fitting quality could be improved if using an indenter with a larger radius to satisfy the conditions of applying this model (Hsueh and Miranda 2004). In this work, the values of $R/a$ of the four coatings on the compliant substrates are larger than unity only when the effective elastic indentation depth is less than 40 nm. That explains why the model fits the data better at a very shallow indentation depth. The fitting quality could also be deteriorated because the tip of the cubic corner is not in a perfect spherical shape even at very front, and the polymeric films do not deform pure elastically but visco-elastically during the indentation. Nevertheless, the model shows the right trend at the lower indentation depth.
5.4.3 Gao’s model - at deeper penetration depths

5.4.3.1 Modeling with a conical indenter

At a larger load and a large indentation depth, the normal indented material unavoidably deforms both elastically and plastically. That is the situation that the Gao’s model was originally developed in order to extract the intrinsic elastic modulus of the coating from the substrate effect at a coating-substrate system.

As discussed in Section 3.2.2.3 in Chapter Three, Gao and his colleagues (Gao, Chiu et al. 1992) proposed that for a conic indenter indenting a coating-substrate system when the indented materials deform both elastically and plastically, the unloading compliance, \( \frac{d\delta}{dF} \), is linearly dependent on the inverse of the plastic indentation depth \( \frac{1}{\delta_p} \) by a material constant \( \frac{1-\nu}{\mu} \), where \( \nu \) is the Poisson ratio and \( \mu \) is the shear modulus (Loubet, Georges et al. 1984):

\[
\frac{d\delta}{dF} = \frac{1}{4\delta_p \tan \theta} \left( \frac{1-\nu}{\mu} \right)_{\text{eff}} \tag{3.11}
\]

Where,

\[
\mu = \frac{E}{2(1+\nu)} \tag{3.12}
\]

\[
\left( \frac{1-\nu}{\mu} \right)_{\text{eff}} = \frac{1-\nu_s-(\nu_c-\nu_s)I_1(t/a)}{\mu_s+(\mu_c-\mu_s)I_0(t/a)} \tag{3.13}
\]

In which, \( \delta_p \) is the plastic indentation depth defined in Figure 3.2, \( F \) is the indentation load, \( E \) is the elastic modulus, \( \mu \) is the shear modulus, \( \nu \) is Passion ratio, \( \theta \) is the enclosed half angle of the core of the indenter, the subscript donation \( \text{eff} \) means the overall “effective” response of the coating-substrate system during the indentation, the subscripts of \( c \) and \( s \) refer to the coating and the substrate respectively. \( I_1 \) and \( I_0 \) are functions of the coating-thickness-to-contact-radius ratio \( t/a \). \( t \) is the coating thickness and \( a \) is the contact radius of the projected indentation contact area. Let \( \xi = t/a \), then,
\[
I_1(\xi) = \frac{2}{\pi} \arctan \xi + \frac{\xi}{\pi} \ln \frac{1+\xi^2}{\xi^2} \quad \text{3.14a}
\]

\[
I_0(\xi) = \frac{2}{\pi} \arctan \xi + \frac{1}{2\pi(1-\nu)} \left[ \xi(1-2\nu) \ln \frac{1+\xi^2}{\xi^2} - \frac{\xi}{1+\xi^2} \right] \quad \text{3.14b}
\]

The value of \( \frac{d\delta}{dF} t \) can be calculated as a function of \( \frac{t}{\delta_p} \) according to Eq. 3.11.

The moduli of the coating and the substrate can be calculated from the slope of the plot between \( \frac{d\delta}{dF} t \) and \( \frac{t}{\delta_p} \) by using Eq. 3.12-3.14.

5.4.3.2 Modeling results

Using a cubic corner indenter with the normal tip radius of 40 nm, the coating-substrate system is indented by the indenter in cubic corner geometry when the indentation depth is over than about 30 nm. The cubic indenter can be treated as a conical indenter with a half enclosed angle of 42.28°, because the contact area between the indenter and the specimen is the same as the cubic indenter at the same indentation depth. Assuming the coating and the substrate materials are impressive, that is \( \nu_{eff} = \nu_c = \nu_s = 0.5 \), the value of \( \frac{d\delta}{dF} t \) can be calculated as a function of \( \frac{t}{\delta_p} \) by varying the ratio of \( E_c / E_s \) according to the Eq. 3.11 and the results were plotted comparing the experimental data as in Figure 5.8 (a-d) for the each stiff coating on the compliant substrate respectively. The empty purple squares are the best fits of the model to the experimental data.
Figure 5-8 $\frac{d\delta}{dF} t$ vs. $t/\delta_p$ for the coatings: (a) 3,000 nm, (b) 220 nm, (c) 125 nm and (d) 47 nm
From Figure 5.8(a-d), the fitting quality is relatively better at smaller of \( t / \delta_p \), that is, at deeper indentation depths especially when the indent crossed the interface of the coating and the substrate. Although, the "true" ratio of \( E_c / E_s \) should be about 2 for the coating-substrate system studied, the model predicted data of \( \frac{d\delta}{dF}t \) at the ratio of \( E_c / E_s \) as 2 are always much larger than the experiment values. And it is interesting to find that the best fitting values for the ratios of \( E_c / E_s \) are 5.94, 10.55, 11.34 and 19.36 for the coatings with thickness of 3,000 nm, 220 nm, 125 nm and 47 nm respectively, as shown in Figure 9.
Figure 5-9  The best fitting ratios of $E_c/E_s$ for the compliant substrate system
From Figure 5.9, the best fitting values of $E_c/E_s$ of the thicker coatings are smaller than the thinner coatings. The possible reason could be that the Gao's model did not take into account the residual stress effect that exists within the coating and between the interfaces (Gao, Chiu et al. 1992). It is believed that the residual stress affects the measurements more significant for a thin coating-substrate system than for a bulk material (Kraft and Nix 1998; Brennan, Munkholm et al. 2000; Swadener, Taljat et al. 2001; Hsueh 2002; Lepienski, Pharr et al. 2004; Malzbender 2004; Malzbender and Steinbrech 2004; Yang 2004). For these SR399 coatings, the residual tension stress is expected to exist, resulting from the spin-coating processes: the solvent vaporization during the spin-coating and the polymer matrix shrinkage when forming densely cross-linking network during an UV curing. Therefore, the stress gradient in a thicker coating should be smaller than a thinner coating. All these factors could be the reasons why the best fitting values of $E_c/E_s$ is larger for the thinner coatings than that of the thicker ones. Therefore, the residual stress needs to be taken into account in Gao’s model, in order to have a better fitting quality for these ultrathin coating-substrate systems.

5.4.4 Korsunsky’s empirical Model

5.4.4.1 Modeling using a sharp pyramidal indenter

The form of a model originally developed for the effective hardness in a coating-substrate system has been adopted by Berasategui and Bull for the effective elastic modulus evaluation. They claimed the model fit surprisingly well with the experimental date for a single-layer and even a double layered coating-substrate systems although there was lack of soundly-based physical origins (Berasategui, Bull et al. 2004). The adopted model for the composite modulus $E_{sys}$ is

$$E_{sys} = E_s + \frac{E_c - E_s}{1 + \beta^2 \frac{t}{\phi}}$$

where $E_{sys}$, $E_c$ and $E_s$ are the effective elastic modulus of the coating-substrate system, the coating elastic modulus and the substrate elastic modulus respectively, $t$ is
thickness of the coating, $\phi$ is a parameter that may relate to the coating fracture and $\beta$ is a fitting parameter (Korsunsky, McGurk et al. 1998).

5.4.4.2 Modeling results

Applying the known intrinsic moduli of the coating and the compliant substrate ($E_s = 2.95 \pm 0.08 \text{ Gpa}$ and $E_c = 6.08 \pm 0.17 \text{GPa}$) in Eq. 3.16, the modeling effective moduli as a function of relative indentation depth, R.I.D., fit fairly well at the indentation depth within the two times of the coating thickness, but once again except for $3 \mu \text{m}$ coating, as shown in Figure 5.10(a-d). The model predicts the effective moduli decrease slightly faster than the experimental values, especially when increasing the coating thickness. The indenter could be too sharp for $3 \mu \text{m}$ coating for applying the model. The fact suggests that an indenter with the tip radius at same dimension order with the coating thickness is necessary in order to apply the model. This premature conclusion is subject for future studying.
Figure 5-10 The experimental and the Korsunsky’s Model results for the coatings:
(a) 47 nm, (b) 125 nm, (c) 220 nm and (d) 3000 nm.
5.5 Summary

Three potential models have been examined to extract the intrinsic elastic modulus for a polymeric stiff coating on a compliant polymeric substrate. The results indicate that the effective modulus of a coating-substrate system depends on the ratio of elastic modulus between a coating and the substrate, the indenter tip size, the coating thickness, the adhesion property and residual stress in a complex way. It is found that the effective modulus of the coating-substrate system depends logarithmically on the ratio of the indentation depth to the coating thickness before any fracture of the coatings occurs.

The Hsueh’s elastic model can fit the experimental data fairly well as long as the indenter remaining the spherical geometry. In order to validate the Gao’s model for submicron polymeric coatings, the residual stress effects of the coatings and the interface between the coating and the substrate need to be taken into account. Although the Korsunsky’s model was surprisingly fitting very well for submicron meter coatings, the theoretical bases are subject to be further investigated. It is suspected that the indenter radius needs be at the same order of dimensions with the coating thickness for the best fittings of the models. Overall speaking, a more applicable model needs to be developed in future for interpreting the elastic response of a stiff coating on a compliant substrate.

5.6 Future work on Modeling for a compliant substrate

It has been shown that it is of academic and practical interest to model the mechanical properties of a coating on a compliant substrate. However, due to the difficulty of defining precisely the stress field, especially across the interfaces, a general theoretical solution has not been developed yet. However, the preliminary study found that, for a submicron polymeric coating on a compliant substrate, the effective moduli have a close logarithmic relationship with the relative indentation depth (R.I.D.)--the ratio of the indentation depth to the coating thickness--within the range of R.I.D. of 2, in a logarithmic coordinate as shown in Figure 5.11. It could be a fundamental information that could be used for developing a numerical solution by a finite element analysis in the future.
Figure 5-11  The effective moduli of submicron polymeric coatings have a logarithmic relationship with R.I.D.
Chapter Six: Nanoindentation-induced delamination of submicron polymeric coatings

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6.1 Introduction

Surface coatings have been widely used in different engineering applications, including scratch-resisting coatings, passivation layers in semiconductor chips and packages, and ceramic thermal barrier coatings for advanced gas turbine engines. For example a scratch-resistant lens coating can improve the longevity of plastic eyeglass lenses, and multilayered ultrathin coatings with unique optical properties can be constructed to improve optical performance. Surface damage and interfacial failure may affect the performance of coating systems and limit the reliability of devices. Thus, reliable characterization of interfacial strength is critical to the improvement of adhesive properties and to the control of quality in a multilayer structure and devices. Accurate and rapid methods for the characterization of ultrathin coatings would be particularly useful to accelerate product development, to improve product design, and to ensure quality control.

There are various methods developed to evaluate the interfacial strength of surface coatings, such as blister tests (Williams 1970; Bennet, Devries et al. 1974; Jensen and Thouless 1993), residual stress-driven delamination tests (Bagchi, Lucas et al. 1994), scratch tests (Wirasate and Boerio 2005) (Huang, Lu et al. 2004) (Zhang, Tsou et al. 2002; Ramsteiner, Jaworek et al. 2003) and indentation tests (Marshall and Evans 1984; Matthewson 1986; Dehm, Ruhle et al. 1997; Vlassak, Drory et al. 1997; Li, Carter et al. 2001; Li, Palacio et al. 2002; Lu and Shinozaki 2002). Although the scratch test is the most popular technique for qualitatively determining the adhesion of various coatings, it may not provide an absolute measurement of the interfacial strength for the coating-substrate interface (Kriese, Gerberich et al. 1999).

The occurrences of changes in the slope and discontinuities in load-displacement curves, the phenomena are called the “pop-in” events or sudden displacement
excursions, are usually related to the phase transition or the indentation-induced delamination (Corcoran, Colton et al. 1997; Bei, Lu et al. 2004; Wang, Qiao et al. 2004). The indentation-induced interfacial crack usually can be propagated in both the loading and unloading processes.

The studies of indentation-induced delamination were focused on the relation between the indentation load and the delamination size. Chiang et al. analyzed the indentation deformation and pointed out that the compressed coating is prone to delaminate from the substrate (Chiang, Marshall et al. 1982). Matthewson further proposed that the radial displacement caused by indentation introduces a shear stress at the interface, which causes the initiation and propagation of adhesive failure (Matthewson 1986). Evans and Hutchinson (Evans and Hutchinson 1984), Marshall and Evans (Marshall and Evans 1984) and Rossington et al. (Rossington, Evans et al. 1984) determined the resistance to interfacial delamination from the studies of the interfacial crack propagation. Ritter et al. have developed a simple model to calculate the fracture energy based on the indentation load versus the delamination size (Ritter, Lardner et al. 1989). Most of these work were on brittle materials or brittle material coatings for their fracture and delamination studies (Marshall and Evans 1984; Kriese, Gerberich et al. 1999). The reason might be that it is hard to determine the exact the fracture dimensions due to the recovery of ductile and elastic materials such as polymers.

Thus, another approach of studying the delamination is to determine the interfacial strength from the indentation loading-unloading curve. Dehm et al. developed an approximate elastic model for the estimation of the interfacial yield strength of a metal film on a ceramic substrate using a conical indenter, in which they neglected the effect of the deformation in the substrate and assumed that the contact between the film and the substrate was frictionless directly under the indentation (Dehm, Ruhle et al. 1997). Lu and Shinozaki extended Dehm’s model to study the indentation of polymeric thin films of poly(methyl methacrylate), polystyrene and high impact polystyrene on a glass substrate using a flat-ended cylindrical indenter, and obtained a critical interfacial shear strength (Lu and Shinozaki 2002). However, there are few studies on the indentation-induced delamination of an ultrathin polymeric coating on a polymeric substrate with similar elastic properties, which likely displays different behavior from soft
coatings on hard substrates. There is a great academic and practical interest to study the interfacial strength of an ultrathin polymeric coating on a compliant substrate.

Studies of thin polymeric films have provided a variety of fascinating and as yet unexplained observations (Jones and Richards 1999), which may be determined by the volume fraction of interfacial region (Teichroeb and Forrest 2003). A well known phenomenon is the reduction in the glass-rubbery transition temperature (Tg) typically for polystyrene (Ellison and Torkelson 2002; Reiter 2002; Ellison and Torkelson 2003; Alcoutlabi and McKenna 2005), which is likely due to the size effect on the equilibrium state of the polymer chains in submicron coatings (Alcoutlabi and McKenna 2005). Using the nanobubble inflation test, O'Connell and McKenna (O'Connell and McKenna 2005) recently examined the viscoelastic properties of ultrathin polymer films of poly(vinyl acetate) (PVAc). They found that the rubbery compliance for the thin film of 27.5 nm in thickness is smaller by a factor of about 320 compared to the bulk material (O'Connell and McKenna 2005), although the mechanism is not understood.

Measurement of the mechanical properties of polymer surfaces is likely to provide an insight into the effects of surface interaction and enable us to evaluate the physical processes controlling the physical behavior of thin polymeric films at the micro- and nano- scales. In principle, there are two basic approaches in assessing mechanical properties of polymer surfaces; a) contact mechanics (Ge, Pu et al. 2000; Fischer 2002; Geng, Yang et al. 2005; Oyen 2005) and b) surface relaxation (Hamdorf and Johannsmann 2000; Hutcheson and McKenna 2005).

It is the purpose of this work to study the effect of the coating thickness on the nanoindentation-induced delamination of submicron polymeric coatings on a polymeric substrate. A quantitative evaluation of the interfacial strength is described. The indentation-induced delamination is analyzed, relating the indentation load at the excursion in the loading curve to the critical interfacial shear stress at which the delamination initiates.

6.2 Analysis of the Indentation-Induced Delamination

Consider a conical indenter being pushed into a bilayer structure as shown in Fig. 6.1. The bilayer structure consists of a thin coating of thickness $h$ and a half-space
substrate. A cylindrical coordinate system is used to describe the deformation of the system, in which the origin of the coordinate system is at the center of the contact zone between the indenter and the surface of the coating, and the $z$-axis is parallel to the loading direction. During indentation, material is pushed away from the indenter and stresses are created in both the thin coating and the substrate. The radial stress in the coating increases with the increase in the indentation depth and eventually causes the delamination of the surface coating from the substrate. As suggested by Dehm et al. (Dehm, Ruhle et al. 1997), the deformation along the radial direction is limited by the ability of the interface to support the radial stress and the transfer of the radial stress can be described by a shear lag model as shown in Fig. 6.1. The delamination is controlled by the interfacial strength between the coating and the substrate. Based on the analysis used by Dehm et al (Dehm, Ruhle et al. 1997), we assume that the contact between the substrate and the coating is frictionless directly under the indentation and the deformation in the coating can be approximated via a depth-independent, i.e. a plane stress-like state so that

$$\sigma^c_{ij}(r,z) = \delta_{ij} \sigma^c_\delta(r) \quad i, j = r, \theta, z \quad \text{for} \quad r < a$$

where $\sigma^c_{ij}$ are the components of stress tensor, the superscript $c$ represents the coating, $\delta_{ij}$ denotes the Kronecker delta with no summation implied in the equation, and $a$ is the contact radius. In general, the relation between the contact radius $a$, and the indentation depth $\delta$, can be expressed as

$$a = a_0 \delta \tan \theta$$

where $a_0$ is a constant depending on the system ($a_0 = 2/\pi$ for the indentation of an elastic half-space (Yang 2004; Geng, Yang et al. 2005) and $a_0 = 3/2$ for the indentation of an incompressible elastic thin film over a rigid substrate with the contact radius much larger than the film thickness (Yang 2003)) and $\theta$ is the half of the included angle of the conic indenter.

The equilibrium equation governing the deformation of the coating under the simplification of plane-stress state is

$$\frac{d^2 u_r^c}{dr^2} + \frac{1}{r} \frac{du_r^c}{dr} - \frac{u_r^c}{r^2} = - \frac{1}{2G^c} \frac{d\sigma_{zz}^c}{dr} \quad \text{for} \quad r < a$$
where $u_r^c$ is the radial displacement in the coating, and $G^c$ and $\nu^c$ are the shear modulus and Poisson ratio of the coating, respectively. The integration of Eq. 6.3 gives

$$u_r^c(r) = Ar - \frac{\nu^c}{2G^c} \int_0^r r \sigma_{zz}^c(r) dr \quad \text{for } r < a$$

6.4

with the constant $A$ to be determined.
Figure 6-1  Schematic of the shear-lag model for the indentation-induced delamination; a) indentation of a bilayer structure consisting of a surface coating and a substrate, b) stress distribution in the coating, c) transfer of the indentation load to the substrate
The radial displacement in the coating is confined by adhesion of the coating to the substrate. According to Agarwal and Raj (Agrawal and Raj 1989), the interfacial shear stress around the contact edge can be approximated in a sinusoidal function as

$$
\tau = \tau_m \sin \left( \frac{\pi r}{2(a+\zeta)} \right) \quad \text{for} \quad a-\zeta < r < a+\zeta
$$

6.5

where $\tau_m$ is the maximum interfacial stress along the interface. The interfacial shear stress rises to the maximum in the regime of $a-\zeta < r < a+\zeta$, in which $2\zeta$ is the size of the influential zone. Considering the force balance at the contact edge, one obtains

$$
\sigma_n(a) = \frac{1}{h} \int_0^{a+\zeta} \tau dr = \frac{2(a+\zeta)\tau_m}{\pi h}
$$

6.6

For a small influential zone, $\zeta << a$, Eq. 6.6 gives

$$
\sigma_n(a) \approx \frac{2a\tau_m}{\pi h}
$$

6.7

Using Eqs. 6.4 and 6.7 and the following equations

$$
\lim_{r \to a} \sigma_{zz}^c(r) = 0
$$

6.8

$$
\sigma_{rr}^c = \frac{2G^c}{1-\nu^c} \left( \frac{du_c}{dr} + \nu^c \frac{u_c}{r} \right)
$$

6.9

and

$$
2\pi \int_0^a r \sigma_{zz}^c(r) dr = F
$$

6.10

one obtains

$$
\frac{a\tau_m}{\pi h} = \frac{G^c}{1-\nu^c} \left( (1+\nu^c)A + \nu^c(1-\nu^c) \frac{F}{4G^c} \pi a^2 \right)
$$

6.11

where $F$ is the indentation load. Solving $A$ from Eq. 6.11 and substituting it into Eq. 6.4, one obtains

$$
u^c(r) = \frac{(1-\nu^c)r}{(1+\nu^c)G^c} \left( \frac{a\tau_m}{\pi h} - \frac{\nu^c F}{4G^c \pi a^2} \right) - \frac{\nu^c}{2G^c} \frac{1}{r} \int_0^r r \sigma_{zz}^c(r) dr \quad \text{for} \quad r < a
$$

6.12

which is the radial displacement in the coating as induced by the indentation.

Considering the mass balance, one has

$$
u^c(a) = \beta \frac{a^2}{h}
$$

6.13
Here, $\beta$ is a constant, which is a function of the mechanical properties of both the coating and the substrate and can be determined by numerical simulation.

From Eq. 6.2 and Eq. 6.13, there is

$$\frac{F}{\delta^3} = \frac{2\pi \alpha^3 G^c \tan^3 \theta}{\nu^c h} \left( (1 - \nu^c) \frac{\tau_{\text{cr}}}{G^c} - (1 + \nu^c) \beta \right)$$

6.14

At the excursion of the indentation-induced delamination, the maximum shear stress is defined as the “critical interfacial shear strength”, $\tau_{\text{cr}}$. Thus, Eq. 6.14 can be re-written as

$$\frac{F_{\text{cr}}}{\delta_{\text{cr}}^3} = \frac{2\pi \alpha^3 G^c \tan^3 \theta}{\nu^c h} \left( (1 - \nu^c) \frac{\tau_{\text{cr}}}{G^c} - (1 + \nu^c) \beta \right)$$

6.15

where $F_{\text{cr}}$ is the critical indentation load and $\delta_{\text{cr}}$ is the corresponding indentation depth.

For the same critical interfacial shear strength and $\beta$, the parameter $F_{\text{cr}} / \delta_{\text{cr}}^3$ is inversely proportional to the thickness of the coating. It should be emphasized that, in deriving Eq. 6.15 the deformation is approximated as a plane-stress like state in the coating and no viscoplastic deformation is taken into account.

Using Eqs. (6.2, 6.13 and 6.15), one obtains the radial displacement in the coating at the edge of the delamination, $\tilde{u}_r(a)$, as

$$\tilde{u}_r(a) = \frac{\beta \nu^c}{2\pi \alpha G^c \tan \theta \delta_{\text{cr}}} \frac{F_{\text{cr}}}{\delta_{\text{cr}}^3} \left( (1 - \nu^c) \frac{\tau_{\text{cr}}}{G^c} - (1 + \nu^c) \beta \right)^{-1}$$

6.16

which is proportional to the ratio of the indentation load to the indentation depth at the delamination. In general, less indentation load is required for the initiation of interfacial delamination in a bilayer system with a thinner surface coating. Thus, less deformation at the delamination is created in the bilayer system with thinner surface coating as indicated in Eq. 6.16.

### 6.3 Delamination of polymeric coatings during indentation

#### 6.3.1 Samples and indentation testing conditions

The polymeric coatings of dipentaerythritol pentaacrylate monomer (Sartomer SR399) were spin-coated on acrylic substrates, which were provided by Optical
Dynamics Corporation (Louisville, KY). The acrylic substrate was a typical material for polymeric lens, with a modulus about one-half that of the SR399. The thicknesses of the polymeric coatings were 47, 125, 220 and 3000 nm, measured by a profilometer (Ambios Technology XP-1, Santa Cruz, CA). All of the coatings were cured for 90 seconds in the presence of CO$_2$ under UV light from a germicidal lamp having an intensity of 4mW/cm$^2$ at 5 cm distance. The sample preparation and polymerization degree are the same as described in Chapter Four and Chapter Five.

The chemistry of the SR399 coatings and the proprietary substrates provided by the ODC was analyzed by Fourier Transform Infrared Spectroscopy (FTIR) (ThermoNicolet Nexus 470) with a resolution of 4 cm$^{-1}$. At room temperature, the spectrum of the SR399 coating on a KBr plate was recorded by a transmission method, and the spectrum of the acrylic substrate was recorded by the attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR). Figure 6.2 shows the characteristic infrared absorptions of the SR399 coating and the acrylic substrate. The carbonyl bond is at 1724-1728 cm$^{-1}$, and the C-O stretching bond at 1270-1150 cm$^{-1}$ (Ichihashi, Henzi et al. 2006). The intensities of the CH=CH stretching at 1407 cm$^{-1}$ and twisting at 809 cm$^{-1}$ are high in the SR399 coating sample due to the residual double bonds in the typical high functional acrylic polymers (Geng, Yang et al. 2005). The SR399 coating has similar chemistry to the surface of the acrylic substrate.
Figure 6-2  Characteristic infrared absorptions of the SR399 coating and the acrylic substrate
The nanoindentation tests were performed in a Hysitron TriboScope (Minneapolis, MN) attached to a Quesant (Agoura Hills, CA) atomic force microscope (AFM). A diamond NorthStar cubic indenter with a nominal tip radius of 40 nm (Minneapolis, MN) was used. Constant loading and unloading rates were used in the indentation tests with the intermediate pause of 2 seconds between the loading phase and the unloading phase. Both the loading and unloading time were 5 s. The indentation depth and applied load were used to evaluate the indentation-induced delamination of the polymeric coatings.

### 6.3.2 Delamination of submicron polymeric coatings

The nanoindentation tests were carried out using the load-control mode with indentation loads within the range of 400 – 5000 μN. Constant loading and unloading rates were used with both the loading and unloading time of 5 s. AFM was used to image selected impression marks. Figure 6.3 shows a typical AFM image of the impression mark indented over the 125 nm coating at the indentation load of 1200 μN and the corresponding morphological profiles of the residual indentation. The indentation profiles are self-similar, and pile-up around the indentation is observed. The highest pile-up occurs at the region close to the center of each side-contact face, while the lowest pile-up occurs at the singular edges of the indentation due to high stress concentration and less elastic recovery. Smooth impression marks are present and no surface cracks are observed. The scans taken along rays a – c are similar as the indenter is triangular symmetry.
Figure 6-3 A typical impression mark and line scans over the indentation profiles for the indentation of 125 nm coating at the indentation load of 1200 μN
A typical example of the loading-unloading curve for the polymeric coatings and the acrylic substrate are shown in Figure 6.4. There is an excursion during the loading phase near an indentation depth of 800 nm for the 125 nm polymeric coating, clearly differing from the indentation of the substrate only. For indentation depths less than 800 nm, larger indentation loads were required for the bilayer-system due to the build up of the stresses in the coating, i.e., more mechanical energy was stored in the coating which eventually led to the delamination of the coating from the substrate. After the delamination, the indentation of the bilayer system is similar in appearance to the indentation in the acrylic substrate. This reveals the similar mechanical properties between the surface coating and the acrylic substrate, as expected, since the elastic modulus of the acrylic substrate is about half of that of the surface coating. The contact stiffness as determined from the upper portion of the unloading curve is slightly smaller for the coating system than that for the substrate only. This is due to the layer structure of the coating system, which has less contact stiffness than each individual system similar to the resultant spring constant for a series connection of two springs. It should be pointed out that there is no excursion for the indentations of the acrylic substrate up to 5000 μN, which strongly suggests that the occurrence of the excursion associates with the interfacial behavior between the surface coating and the substrate. Based on the impression mark as shown in Figure 6.3, it can be concluded that the excursion is likely due to the delamination of the coating from the substrate as suggested in previous discussion.
Figure 6-4  Typical indentation loading-unloading curves for the indentation of 125 nm surface coating and the acrylic substrate
To evaluate the effect of the loading rate on the indentation-induced delamination, different peak loads were applied to the indenter. Figure 6.5 shows the loading-unloading curves for the indentation of the 125 nm polymeric coating subjected to 5 different peak loads of 400, 800, 1200, 1600 and 2000 μN. The indentation load and indentation depth for the excursion behavior are $696.3 \pm 24.1 \, \mu N$ and $829.9 \pm 13.2 \, \text{nm}$, respectively, independent of the loading rate. Thus, the indentation load for the presence of the excursion is the critical load for the indentation-induced delamination of the 125 nm polymeric coating. Also, there is only one excursion present for the indentation loads up to 2000 μN.
Figure 6-5  Effect of the peak indentation load on the “excursion” behavior in the indentation of 125 nm surface coating
In general, the loading stiffness defined as $dF/d\delta$ is a smooth function of the indentation depth. It is expected that, at the excursion, there will be a change in the loading stiffness representing the occurrence of the indentation-induced delamination. Figure 6.6 shows the dependence of the loading stiffness on the indentation depth for three polymeric coatings of 47, 125 and 220 nm. Significant change in the loading stiffness near the excursion is observed for the polymeric coatings of 125 and 220 nm, while less change is found for the polymeric coating of 47 nm. This is likely due to the lower deformation required for the initiation of delamination in thin coatings while more deformation is required for thick coatings, i.e. higher indentation load is required to cause delamination in thick coatings, as discussed in the previous section. It should be pointed out that it is very difficult to determine exactly the critical indentation depth for the polymeric coating of 47 nm. The location for the excursion in the 47 nm coating is best estimated from the change in the slope of the loading stiffness-depth curve.

Figure 6.7 shows the dependence of the critical indentation load for the initiation of delamination on the thickness of the polymeric coatings. A linear relation is observed between the parameter, $F_{cr}/\delta_{cr}^3$, and the reciprocal of the coating thickness, which supports Eq. 6.15. Eq. 6.15 is not applicable for $1/h \to 0$ since a plane stress state was used in the derivation.

In the previous work (Geng, Yang et al. 2005), we characterized the elastic modulus of ultrathin polymer coatings of the densely cross-linked ultrathin dipentaerythritol pentaacrylate (Sartomer SR399) with the thicknesses of 47, 125 and 3000 nm. The coatings were coated on the silicon substrates. We avoided viscoelastic effect on the reduced contact modulus by holding the peak indentation load for 2 seconds over the total indentation period of 12 seconds. It would be expected that the viscoelastic deformation would not have a strong influence on the indentation deformation in the experimental conditions.
Figure 6-6  Dependence of the loading stiffness on the indentation depth for three polymeric coatings of 47, 125 and 220 nm
We applied the same technique in the indentations of the polymeric bilayer structures and did not observe the viscoelastic effect on the reduced contact modulus and the size effect. Using the unloading curves for the indentations of the 3000 nm polymeric coating and assuming the Poisson ratio of the polymeric coatings to be 0.4, one obtains Young’s modulus of 5.13 GPa. In general, one can approximate the cubic indenter as a conical indenter with a half included angle of $42.28^\circ$ (this conical indenter would have the same depth to area ratio as the cubic indenter). On the basis of ultrathin surface coatings over a soft substrate, one can approximate the system as a homogeneous half-space structure and assume $\alpha \approx \frac{2}{\pi}$ and $\beta \approx 0$. Using Eq. 6.15 and the slope in Figure 6.7, one obtains the interfacial strength as 70.35 MPa.
Figure 6-7  Dependence of the critical indentation load on the thickness of the polymeric coatings
6.3.3 Delamination of micron polymeric coatings

For comparison, the same tests were applied on the 3000 nm polymeric coating, and the indentation-induced delamination was also observed in the experiment. Figure 6.8 shows the dependence of the loading stiffness on the indentation depth. There are four excursions in the loading curve of the thick coating system. The deepest indentation depth, corresponding to the 4th delamination event, is 1305 nm, about 2/5 time of the coating thickness, suggesting the stress state in the coating can not be approximated as a plane-stress state and three-dimensional analysis involving the use of numerical simulation is needed to determine the deformation field. The multiple excursions are likely due to the arrest of the interfacial crack, i.e. the indentation closes the interfacial crack after the onset of the indentation-induced interfacial delamination. There is no enough driving force to cause the further propagation of the interfacial crack. The radial stress along the interface then increases with continuous indentation. Once the radial stress reaches the critical interfacial strength, the interfacial delamination occurs again.

The dependence of the critical indentation load on the corresponding indentation depth is shown in Figure 6.9 for the 3000 nm polymeric coating. Higher indentation load is required to cause the initiation of an interfacial delamination of larger size, as expected. A linear relationship between the critical indentation load and the corresponding indentation depth is obtained. Such a relation provides us a potential mechanism to determine the interfacial strength for thick surface coatings deposited on compliant substrates. However, a new model is needed for evaluating the indentation-induced delamination in thick coatings, which may require the use of numerical simulation.
Loading stiffness (μN/nm) vs. Indentation depth ($10^3$ nm)

3000 nm surface coating

"pop-in"

Figure 6-8  Dependence of the loading stiffness on the indentation depth for the polymeric coating of 3000 nm at the peak load of 5000 μN
Figure 6-9  Correlation between the critical indentation load and the corresponding indentation depth for the indentation-induced delamination in the polymeric coating of 3000 nm
6.4 Summary

Indentation-induced delamination provides a unique approach to evaluate the interfacial strength between a surface coating and a compliant substrate. Assuming that the contact radius is much larger than the thickness of the surface coating, we approximate the deformation behavior of the thin surface coating as a plane stress-like state. Using a shear-lag model, we have established a relationship between the critical indentation load and the interfacial strength at which interfacial delamination initiates. The ratio of the critical indentation load to the cube of the corresponding indentation depth turns out to be a linear function of the reciprocal of the coating thickness.

The indentation-induced delamination of a crosslinked polymer ultrathin surface coating over an acrylic substrate has been evaluated using the nanoindentation technique over the range of the indentation loads from 400 μN to 2000 μN for the coating thicknesses of 47, 125 and 220 nm, and over the range of the indentation loads from 400 μN to 5000 μN for the coating thickness of 3000 nm. For the submicron coatings with the thicknesses of 47, 125 and 220 nm, only one excursion phenomenon is observed in the loading phase, suggesting the arrest of the interfacial crack for deep indentations. The dependence of the critical indentation load on the coating thickness agrees with the proposed model. The interfacial strength is found to be 70.35 MPa. Differing from the indentation behavior of the submicron coatings, the 3000 nm polymeric coating displays multiple excursions in the loading curve. This is due to the arrest of interfacial crack during the indentation and the increase of the radial stress with further indentation. Once the radial stress reaches the interfacial strength, the interfacial delamination is initiated again. It should be pointed out that a new model is needed for evaluating the indentation-induced delamination in thick coatings, which may require the use of numerical simulation.
Chapter Seven: Mechanical comparison of a polymer nanocomposite to a ceramic thin film anti-reflective filter

(This chapter is based on the following reference: *Nanotechnology*, Volume 17, 2006, Pages 3584-3590.)

7.1 Introduction

Thin-film optical filters have been produced for over a century and chemical vapor deposition techniques have predominately been the manufacturing industry’s choice. The technique generally includes the deposition of metal-oxide ¼ wavelength thin-film layers of varying refractive indexes to change the optical efficiency of the surface of a substrate. These can include broad band antireflective and reflective coatings as well as edge and band gap filters (Macleod 2001). Antireflection coatings that absorb the visible spectrum (380 nm to 780 nm) are the predominant applications with uses in ophthalmic lenses, solar cells, data storage and other optical devices requiring high optical transmissions.

Traditional vacuum deposited anti-reflective coatings have been made since the 1930’s and have actually performed well when coated on a glass ophthalmic lens, since the coatings themselves were ceramic. During the 1970’s manufacturing improvements allowed for polymer lenses to gain general acceptance as an alternative for glass; however, anti-reflective coatings did not fare well on plastic substrates due to the major differences in the strain behavior of the coating and the lens. The differences in strain behavior between ceramic coatings and plastic lenses are important for both mechanical stresses as well as thermal stresses that can arise when there are large changes in temperature. Thermal stresses occur because of the differences in thermal expansion coefficients. Significant progress has been made in this technology, but the transfer of stresses across the material interface continues to be an issue. Spin on glass coatings via the sol-gel process and hybrid materials including Oromosils have also been proposed, but these have not gained acceptance in the marketplace.

Surface damage to an optical article can induce transmission loss by scattering the incident light. The light scatter is evident as haze, which increases with the surface
roughness and when debonding occurs. A brittle material will exhibit fracture features including voids, cracks, crazing and debonding, whereas ductile material damage is smooth in nature (Xiang, Sue et al. 2001). Debonding can lead to further damage as humidity changes and to further stress at the interfacial boundaries. Cracks and voids can act as stress risers, giving way to further damage. These surface defects can also arise from large differences in the thermal expansion coefficients and ultimate strains between the layers and the substrate. These large strain domain differences can also reduce the resilience of the final article, reducing the impact resistance. In other words, layered coatings are subject to the same problems as conventional composites, in which the interface, the differences in mechanical properties, and the differences in thermal properties all contribute to the design challenges.

The goal of this work was to compare the mechanical performance of an anti-reflective article featuring a proprietary polymer nanocomposite system to an anti-reflective coating deposited onto a polymer substrate using traditional vacuum deposition techniques. The method outlined here represents a low cost solution to create an anti-reflective article that more closely matches the strain performance of the anti-reflective layers to the polymer substrate. The coatings are first applied to a mold in reverse order using a spin coating technique, and then the molds are assembled to create a lens cavity. A low viscosity monomer is introduced in between the two surfaces and cured, at which point the coatings are cured to the substrate. The molds are then removed, leaving a plastic anti-reflective article (Buazza and Sun 2003).

The nanocomposite layers used for this thin-film filter consist of a hybrid polymer with metal oxide nanoparticles (Mennig, Oliveira et al. 1999; Mennig, Oliveira et al. 1999; Krogman, Druffel et al. 2005). The nanoparticles are used to engineer the refractive index and the mechanical properties of the layers. The in-mold method creates a chemical bond between the layers and the substrate. There has been work in which an AR coating based on sol-gel technology has been applied to an optical article using spin coating (Imai, Awazu et al. 1997; Oliveira, Krug et al. 1997), but this method often requires a higher temperature bake out, and there remains an issue with the adhesion to the substrate.
In the last decade, nanoindentation and nanoscratch techniques have proven to be powerful tools in characterizing thin films (Oliver and Pharr 1992; Bushan and Li 2003). There has appeared much work in the analysis of polymer films on metal substrates (Malzbender, den Toonder et al. 2002; Geng, Yang et al. 2005), polymer films on polymer substrates (Soloukhin, Posthumus et al. 2002; Charitidis, Gioti et al. 2004) and multi-layered films on metal substrates (Gao, Chiu et al. 1992; Chudoba, Schwarzer et al. 2000). In this work, a multi-layered film system, consisting of both organic and inorganic materials on a polymer substrate having a total thickness of approximately 300 – 330 nm, was studied. These films are compared using nanoindentation and nanoscratch tests to assess the mechanical performance of the end product. In addition, SEM images of the indentations and scratches are presented to help further explain the failures.

7.2 Experimental details

7.2.1 Sample preparation

In order to compare these two types of anti-reflective thin films, both substrates used were an acrylic flat made by Optical Dynamics Corporation. One set was then coated using a traditional vacuum deposition technique (ceramic), having a total thickness of approximately 330 nm. A second set was made using the in-mold casting technology (nanocomposite) which yields an anti-reflective thin film approximately 300 nm thick as described in the following paragraphs.

The anti-reflective layers are first applied to the molds in reverse order using a spin coater by Optical Dynamics Corporation. The air entering the coater is HEPA-filtered to keep defects to a minimum. The machine first cleans the molds using a high pressure water wash to remove any fine contaminants on the molds. Each layer of the stack is coated onto a glass mold using the spin coating technique, which is a simple and efficient method for depositing uniform thin films on a substrate. This well understood technique controls the layer thickness by balancing the centrifugal forces of a developing thin film to the viscous forces that increase as evaporation takes place (Meyerhofer 1978; Bornside, Macosko et al. 1989). The repeatability of this method is extremely high as long as the coating environment is controlled so that the evaporation...
rate stays constant. This is accomplished by regulating the temperature of the coating chamber and also by exhausting solvent rich air out of the coating bowl.

After the solvent is evaporated, a thin film on the order of a $\frac{1}{4}$ wavelength made of a UV-curable monomer and nanoparticles remains. The layer is then partially cured using a pulse Xenon UV source lamp, leaving an under-cured polymer nanoparticle composite. Subsequent layers are then added on top of the previous layer to build the anti-reflective stack in reverse order. Each mold is processed through the machine in about ten minutes.

The reverse coated molds are then assembled as shown in Figure 2.11, and a low viscosity monomer is introduced into the system. The monomer is then cured using a UV source and heat, a process that takes a total of ten minutes. During this time, the curing of the anti-reflective layers is completed, which creates a very strong bond between the layers and the polymer lens. When the cure is complete, the molds are removed in a water bath, and the lens is cleaned and placed into a low temperature oven and annealed. The final product has the surface qualities of the mold itself; therefore, the article does not need any post processing to complete the prescription.

7.2.2 Sample analysis methods

7.2.2.1 Surface roughness

Some research indicates that surface roughness can affect the apparent contact area of an indenter, an important parameter in the theoretical analysis of surface stress (Bouzakis, Michailidis et al. 2002; Han, Saha et al. 2006). In order to confirm that the surface roughness of the specimens does not violate the assumptions, the surfaces were mapped using a Quesant (Agoura Hills, CA) atomic force microscope (AFM).

7.2.2.2 Nanoindentation test

The nanoindentation tests were performed in a Hysitron Triboscope (Minneapolis, MN) using a diamond NorthStar cubic indenter with a nominal tip radius of 40 nm (Minneapolis, MN). The indentation tests were carried out using a load control mode with the indentation loads up to 6000 $\mu$N at a rate of up to 1200 $\mu$N/s. Using the methods developed by Oliver and Pharr (Oliver and Pharr 1992), the reduced modulus
E_r was obtained from the indentation load-displacement curves as described in Chapter Three.

### 7.2.2.3 Scratching test

Nanoscratch tests were performed in a Hysitron Triboscope (Minneapolis, MN) using a diamond NorthStar cubic indenter with a nominal tip radius of 40 nm (Minneapolis, MN). The scratch was made with one sharp edge of the indenter orientated in the direction of travel (point-on orientation) and the applied normal load was increased linearly to the maximum load (ramp mode) with the indenter moving along at the speed of 1/3 \( \mu \text{m/second} \). The maximum scratching distance was 10 \( \mu \text{m} \). The normal and lateral forces of the indenter were monitored during the scratch with specific attention to discontinuities in the lateral force curve indicating stresses exceeding the yield and ultimate stresses.

The stress distribution during a scratch has been evaluated by Xiang and results in sharp increases in the material’s tensile stresses on the trailing edge of the stylus (Xiang, Sue et al. 2001). Again a glassy material does not exhibit high tensile strength and the tensile failures along with shear rupture during a scratch would be expected. The two types of failures expected during the scratch for glassy materials would be ductile and brittle (Briscoe, Pelillo et al. 1996; Wong, Sue et al. 2004). In a plastic failure, the material is strained beyond the yielding limit in shear and should leave a relatively smooth scratch, although there may be some tearing. A brittle failure pushes the stresses beyond the tensile yield and will exhibit sharp cracks in the trough as well as a very rough lateral force scan.

### 7.3 Surface roughness

Images from the AFM depicting the surface roughness of the two films are shown in Figure 7.1. The columnar surface profile of the traditional vacuum deposition is evident in the image, but the surface roughness of each sample is on the order of a few nanometers and should not affect the indentation and scratch tests (Wong, Sue et al. 2004). The average surface roughness \( R_s \), the deviation of surface height from the
mean plane, of the polymer nanocomposite film was 4.00 nm (Fig.7.1(a)) and 6.42 nm for the vacuum deposited ceramic film (Fig.7.1(b)).
Figure 7-1  AFM Surface maps of (a) the nanocomposite sample (Ra: 4.00 nm) and (b) the ceramic sample (Ra: 6.42 nm).
7.4 Coating fractures

7.4.1 Fracture phenomena

For large indentation loads, glassy materials may exhibit cracking during the indentation process (Malzbender, den Toonder et al. 2002; Rhee, Kim et al. 2002). There are several types of cracking that may occur during the indentation. Radial cracks are common for sharp indenters and extend outward from the edges of the indenter, while cone cracks occur circumferentially around the indentation. Both types of cracks can be detected by sharp changes in the slope (stiffness) of the force displacement curves during the indentation. This stiffness will have large discontinuities as strain energy is released during fractures. The AFM attached to the indenter does not have the resolution to accurately depict any cracking that may have occurred, so the indentation was analyzed using a Hitachi-3200 SEM. This required a careful indexing plan so that surface fractures could be found quickly when the sample was moved. There are several models for the computation of the fracture toughness based on the size of the crack dimensions. In this work, only the critical load at which cracking occurs will be considered, which is seen as a discontinuity in the load displacement curve during the indentation.

7.4.2 Fractures induced by nanoindentation

Several nanoindentations were performed on each sample, and the hardness and the reduced elastic modulus were plotted against the indentation contact depth (Fig. 7.2). As expected, the curves straighten out as the indentations start to enter the substrate, and at about 500 nm, each sample exhibits more or less the same reduced modulus as shown in Figure 7.2(a). The difference in the mechanical properties is in the hardness, where the ceramic sample is three times as hard as the nanocomposite sample in Figure 7.2(b), which again is not a surprising result. What is interesting to note is that the comparison of the bulk properties of the materials does not line up with the measured reduced modulus. This can be explained by the relatively soft substrate, which was included in the analysis as it is a part of the finished article, and as such needs to be included.
The more interesting data from the nanoindentation is the load displacement curves (Fig. 7.3), in which the ceramic sample shows several discontinuities during the loading phase that can be attributed to a brittle failure (Fig. 7.3(a)). These indentation-induced failures consistently occur at the multiple penetration depths of around 530 nm, 1020 nm, 1720 nm and 2200 nm. These are more clearly illustrated by the stiffness curve as a function of indentation depth (Fig. 7.4 (a)). This failure does not show up with the nanocomposite sample (Fig.4(b)), and to make sure that it was not hidden, we also took the derivative of the loading curve to determine whether there was a jump in the stiffness, which we did not see (Fig. 7.4(b)).
Figure 7-2  (a) The reduced elastic modulus and (b) hardness of two samples as a function of indentation depth
Figure 7-3  Indentation load-displacement curves of (a) the ceramic sample and (b) the nanocomposite sample
Figure 7-4  Stiffness of (a) the ceramic and (b) the nanocomposite samples at indentation load of 6000 \( \mu \)N
In order to verify their cracking behavior, the samples were analyzed under a SEM as shown in Figure 7.5. The nanocomposite sample shows no cracking either radially from the edges of the cubic indenter, or concentrically around the point of indentation (Fig. 7.5(b)). From these results and the load displacement curves, we can say with much certainty that the indentation is purely plastic/elastic and that there is no delamination from the substrate. The ceramic sample does show cracks emanating radially outward from the edges of the indenter as well as circumferential cracks (Fig. 7.5(a)). We cannot determine from this data whether the zone cracking has initiated a delamination, although this is probable due to the probable strain density at the interface.

The other interesting phenomenon exhibited by the nanocomposite sample is the elastic response to the indentation. Upon closer focus of the indentation imprint (Fig. 7.6) we noticed that at the edge of the Berkovich tip there was some localized plastic failure with elastic recovery. This is quite interesting, in that the nanocomposite sample exhibits the ability to absorb the indentation elastically without a failure. The nanocomposite coating is 0.33 μm in thickness. Based on the 1 μm scale of Figure 7.6, the bridging between the crack surfaces appears to within the coating, not the underlying substrate.
Figure 7-5  SEM images of indentation for (a) the ceramic sample and (b) the nanocomposite sample at an indentation load of 6000 μN
Figure 7-6 Close up of the nanocomposite indentation
7.4.3 Fractures induced by nanoscratching tests

Nanoscratch tests showed responses similar to those of the indentation tests; the response of the nanocomposite sample was purely plastic/elastic and the ceramic sample exhibited brittle failures. In each case, the lateral force curves show deviation from the linearly applied normal force (Fig. 7.7). The reduction of the lateral force is attributed directly to the release of strain energy due to a plastic or a brittle failure. The ceramic sample exhibits much sharper transitions in the lateral forces that increase periodically as the scratch load is increased, and consequently the normal displacement (the penetration depth) increases (Fig. 7.7(a)). This would be expected of a ceramic material with small ultimate strains causing tensile failures at the trailing edge of the stylus. The elastic response of the nanocomposite sample has a smoother lateral force curve (Fig. 7.7(b)).

As with the indentations, we took images of the scratch using an SEM to confirm the response (Fig. 7.8). The ceramic sample exhibits a classic snapshot of brittle cracking due to tensile failures at the trailing edge of the indenter (Fig.7.8(a)). The nanocomposite exhibits failures that look plastic in nature, in other words the bottom of the trough is smooth with a rough edge (Fig. 7.8(b)).
Figure 7-7  Nanoscratch lateral force curves for (a) the ceramic and (b) the nanocomposite samples at the maximum load of 1000 μN as a function of the scratch depth
Figure 7-8 SEM images of scratch for (a) the ceramic sample and (b) the nanocomposite sample
7.5 Summary

In this study, we have compared the mechanical response of a newer technology for applying an anti-reflective thin-film filter to an optical article to a well established technology. In particular, we have concentrated on common surface failures of the final product, which include scratching, delamination and crazing (commonly occurring with rapid strain fluctuations). These failures lead to light scattering, which reduces the optical efficiencies of the thin-film filters. In this study, the ceramic film failures resulted in rougher surface damage, which should lead to more haze. The newer technology outlined here is designed to more closely match the elastic properties of the substrate, thus eliminating many of these issues and minimizing damage done to the final article.
Chapter Eight : Kinetics of UV polymerization

The preliminary project on fabricating AR lenses with nanocomposites has been completed and the initial marketing is promising. However, it is just the first stage of the project to develop nanocomposite AR coatings by this in-mold spin-coating process. There are a number of areas that need to be pursued in order to make more perfect AR lenses with improved optical and mechanical performances in the future. The major tasks include: (1) to make well dispersed metal oxide nanoparticles with high reflective indexes and high mechanical properties, (2) to select fast and strong UV curable monomers and understand their curing kinetics, (3) to develop mechanical characterization methodologies, especially when using a compliant substrate, (4) to modify spin-coating processes for repeatable and defect-free coatings and (5) to optimize the design of the layered structure for the best optical and mechanical properties. This dissertation has already partially completed some of these important tasks, which include modeling the kinetics of UV polymerization of an ultrathin coating.

8.1 Background of UV polymerization

An UV polymerization process needs to be pursued fundamentally in order to achieve fast reactions, controllable monomer conversions, uniformity across the coating, optimal mechanical properties and to eliminate the spin-coating defects such as striations for the ODC’s AR lens fabrication.

Preliminary experimental results show that UV polymerizations are significantly affected by monomer type and functionality, photoinitiator type and amount, UV source, metal oxide nanoparticles inside, residual solvents and environmental gases. For example, pentafunctional acrylate monomer Sartomer® SR399 can be polymerized under UV radiation without a photoinitiator; the polymerization rate is faster in CO₂ than in air due to the O₂ inhibition; and the CeO₂ or TiO₂ nanoparticles slow down the rate and reduce the conversions of [C=C] at the time scale allowed. These FTIR measurements of [C=C] levels have been previously shown in Figure 2.4.

Therefore, the polymerization under UV radiation is a complex reaction with key rate-limiting mechanisms that include: (1) UV initiated monomer polymerizations without
photoinitiators, (2) UV polymerization with photoinitiators, (3) thermal induced reactions with initiators and (4) thermal induced reactions without initiators. Oxygen inhibition, free radical transfer to solvent, metal oxide catalytic effects, and the Trommsdorf effect also influence the overall polymerization rates.

For these reasons, it is of academic and practical interest to further study the UV polymerization process of this ultrathin nanocomposite coatings composed of metal oxide nanoparticles. A fundamental, mechanism-based approach to modeling these issues is necessary, and the individual differential equations corresponding to each mechanism will be approximated. The goal of this work is to identify the rate limiting steps, determine how these vary during polymerization, and then to optimize the coating formulation and the UV polymerization conditions. Maple 9.5, Fluent and Femlab could be used as the software for this modeling work.

8.2 Analysis of the UV polymerization process

From the Beer-Lambert law (Decker 1992), the local light intensity across the coating $I$ is a function of the distance from the coating surface or the amount of absorption along the light path is:

$$ I = I_0 e^{-(H-Z)(\varepsilon_{MO}[MO]+\varepsilon_{PI}[PI]+\varepsilon_{M}[M])} = I_0 e^{-\psi(H-Z)} $$

8.1

Where we define,

$$ \psi = \varepsilon_{MO}[MO] + \varepsilon_{PI}[PI] + \varepsilon_{M}[M] $$

8.2

In which, $\varepsilon_{PI}$, $\varepsilon_{MO}$ and $\varepsilon_{M}$ are the extinction coefficients of the photoinitiator, metal oxide nanoparticles and monomers respectively, measured and calculated from the UV-Vis spectra; $[PI]$, $[MO]$ and $[M]$ are concentrations of the photoinitiator, metal oxide nanoparticles and monomers respectively; $h$ is the thickness of the coating; and $Z$ is the depth in the coating ($Z=0$ at the bottom, $Z \leq h$).

Applying Equation 8.1, the local UV intensity of a nanocomposite coating can be estimated. For example, for a model system of SR399/Irgacure184/CeO$_2$ with CeO$_2$ weight concentrations of 0, 40% and 80%, assuming the incident UV intensity $I_0$ is 444mW/cm$^2$ (4,440 W/m$^2$) and the coating thickness $H$ is 100 nm ($10^{-7}$ meter), then, the local UV intensity in a coating can be calculated as plotted in Figure 8.1. It is clear
that even for a coating at a thickness of only 100 nm, the CeO$_2$ nanoparticles significantly absorb UV lights inside the coating, and consequently the UV polymerization process is expected to be affected.

The model included the individual reaction steps of initiation, propagation and termination, with special emphasis on initiation and termination. The quasi-steady state assumption (QSSA) can be applied to the overall free radical balance (leading to the need to find the roots of the polynomial expressions), or can be ignored by writing the differential equation for all free radicals and numerically solving them. The propagation equation is straightforward if the byproduct reactions are not considered for simplicity.
Figure 8-1 The local UV intensities of SR399/Irgacure184/CeO$_2$ coatings

(CeO$_2$ is weight percentage with respect to SR399)
8.2.1 Initiation

8.2.1.1 Photoinitiator decomposition (UV+PI)

Photolysis process of photoinitiator obeys a first-order kinetic law (Decker 1992),

\[
\ln \left( \frac{[PI]_t}{[PI]_0} \right) = -k_{d,PI} t
\]

8.3

Thus,

\[
[PI]_t = [PI]_0 e^{-k_{d,PI} t}
\]

8.4

In which, \([PI]_0\) and \([PI]_t\) are the photoinitiator's initial concentration and the concentration at the time \(t\), \(k_{d,PI}\) is the dissociation constant of the photoinitiator and it is a function of local UV intensity. For example, \(k_{d,PI}\) for photoinitiator Irgacure 369 is (Abadie and Appelt 1987; Decker 1992),

\[
k_{d,PI} = 0.0044I + 0.0018 = 0.0044I_0 e^{-\psi(h-Z)} + 0.0018
\]

8.5

In this empirical equation 8.5, the units of the photoinitiator's dissociation constant \(k_{d,PI}\), the UV light intensity \(I\), \(\psi\), \(h\) and \(Z\) are \(s^{-1}\), \(mW/cm^2\), \(cm^{-1}\) and \(cm\) respectively. If the function of Eq. 8.5 could be approximated for the dissociation of photoinitiator Irgacure 184, then the residual photoinitiator concentration across the coating of 80%CeO2/SR399/Irgacure184 can be predicted after exposure to UV, as shown in Figure 8.2 (a) varying with time and distance from the coating surface (3D image) and (b) decreasing with time at the coating surface and bottom (2D image).
Figure 8-2 Irgacure 184 dissociating rate with time $t$ at a location $Z$ (a) and with time $t$ at coating surface and bottom (b).
In general, one photoinitiator molecule dissociates into two free radicals. The initiation rate is,

\[ PI \xrightarrow{h\nu} 2R^* \]  

\[ \frac{d[M^*]}{dt} = -\frac{d[PI]}{dt} = 2\phi k_{d,PI} [PI]_0 e^{-k_{d,PI}t} \]

In which, \( R^* \) is a free radical dissociated from an initiator, \([M^*]\) is the molecular free radical concentration, \( \phi \) is the quantum yield of the photoinitiator dissociation efficiency under UV radiation (usually, 0.01-0.1).

### 8.2.1.2 UV polymerization without photoinitiators (UV+no PI)

In Figure 2.4, it has been proven that some acrylic monomers, such as SR399, could be polymerized under UV radiation without a photoinitiator. The temperature of the coating is estimated less than 70°C during the normal radiation conditions applied. This reaction is likely initiated by the activated monomers after the absorption of quantum photon energy. The process could be a bimolecular process. Then, the polymerization rate \( R_i \) is,

\[ R_i = -\frac{d[M]}{dt} = k_{p,\lambda-noPI} \left( \frac{k_{i,\lambda-noPI}}{2k_{t,\lambda-noPI}} \right)^{0.5} [M]^2 = A[M]^2 \]  

Define, \( A = k_{p,\lambda-noPI} \left( \frac{k_{i,\lambda-noPI}}{2k_{t,\lambda-noPI}} \right)^{0.5} \)  

in which, \( k_{p,\lambda-noPI} \), \( k_{i,\lambda-noPI} \) and \( k_{t,\lambda-noPI} \) are the propagation constant, the initiation constant and the termination constant of the reaction respectively, and \([M]\) is the monomer concentration (more precisely, the [C=C] concentration if it is a multifunctional acrylic monomer).

Integrating Equation 8.8, we have,

\[ [M]_t = \frac{1}{At + \frac{1}{[M]_0}} = \frac{[M]_0}{At[M]_0 + 1} \]  

or,
\[
\frac{[M]_t}{[M]_0} = \frac{1}{At[M]_0 + 1}
\]

Where, \([M]_t\) and \([M]_0\) are the monomer concentration at time \(t\) and the initial concentration respectively.

A 100 nm SR399 coating was radiated at an intensity of 4mW/cm\(^2\) in the presence of CO\(_2\). The polymerization degree or [C=C] conversion rate was monitored by Fourier Transform Infrared Spectroscopy (FTIR) at 64 scans and resolution 4 cm\(^{-1}\) with Mattson Galaxy Series 3000 (Madison, WI). In Figure 8.3, the experimental data are plotted and fitted to Equation 8.10. It is apparent that the model results have the same trend as the experimental data; thus, the mechanism of a bimolecular reaction or a 2\(^{nd}\) order reaction could be the right assumption. The parameter \(A\), of the value of 4.1599E-07, can be determined by the best data fitting as shown in Figure 8.3.
Figure 8-3  UV polymerization rate of SR399 without photoinitiators
The free radicals could be generated due to the interaction between two monomer molecules stimulated by UV radiation (a bimolecular reaction). If so, the initiation could be expressed as:

\[
M + M \xrightarrow{h\nu} 2[M^*] \tag{8.12}
\]

\[
\frac{d[M^*]}{dt} = 2k_{d,\lambda}\phi_2(1 - e^{-\psi(H-Z)})[M]^2 \tag{8.13}
\]

Where \(k_{d,\lambda}\) is the dissociation constant of the free radicals generated by UV radiation, \(\phi_2\) is the quantum yield of the monomer dissociation under the UV radiation, and \(\psi\) is the absorption function of the composition defined as in Equation 8.2.

### 8.2.1.3 Thermal polymerization with photoinitiators (PI)

\[
PI \xrightarrow{\text{heat}} 2R^* \tag{8.14}
\]

\[
\frac{d[M^*]}{dt} = 2f_1k_{d,\lambda-PI}[PI] \tag{8.15}
\]

In which, \(f_1\) is the efficiency of a free radical initiating a polymerization, and \(k_{d,\lambda-PI}\) is the initiation constant of a heat polymerization with photoinitiators.

### 8.2.1.4 Thermal polymerization without photoinitiators (Heat+no PI)

The reaction could be important if the temperature is much higher than a room temperature. The polymerization initiation process can be presented as,

\[
M + M \xrightarrow{\text{heat}} 2[M^*] \tag{8.16}
\]

\[
\frac{d[M^*]}{dt} = 2k_{d,t\lambda}\phi_2[M]^2 \tag{8.17}
\]

In which, \(f_2\) is the efficiency of a free radical initiating a polymerization, and \(k_{d,t}\) is the initiation constant of a heat polymerization without photoinitiators.

Comparing with the UV polymerization without photoinitiators, the reaction mechanism of thermal polymerization without photoinitiators could be similar, but since the energy sources are different, UV radiation may cause the polymerization at surface faster than at the bottom.
Considering all above factors, the overall initiation rate is

\[ \frac{d[M^*]}{dt}_{\text{overall}} = \frac{d[M^*]}{dt}_{\text{UV+PI}} + \frac{d[M^*]}{dt}_{\text{UV+noPI}} + \frac{d[M^*]}{dt}_{\text{heat+PI}} + \frac{d[M^*]}{dt}_{\text{heat+noPI}} \]  

Equation 8.18

Since the temperature of the coating is less than \(70^\circ\text{C}\), the Equation 8.18 can be simplified by only considering the UV radiation effect. That is,

\[ \frac{d[M^*]}{dt}_{\text{overall}} = \frac{d[M^*]}{dt}_{\text{UV+PI}} + \frac{d[M^*]}{dt}_{\text{UV+noPI}} \]  

Equation 8.19

### 8.2.2 Propagation

#### 8.2.2.1 Chain growth

After initiation, the large molecular free radicals continue to growth by adding new monomers.

\[ nM^* + M \rightarrow (n+1)M^* \]  

Equation 8.20

\[ R_p = \frac{-d[M]}{dt} = k_p[M][M^*] \]  

Equation 8.21

In which, \( R_p \) is the chain propagation rate, and \( k_p \) is the chain propagation constant.

#### 8.2.2.2 Chain transfer

During the chain growth, large molecular free radicals could also transfer to the photoinitiator, monomer and residual-solvent molecules. Consequently, these side reactions will reduce the initiator efficiency and the overall molecular weight. These chain transfer reactions, such as those transferring to solvent molecules, can be expressed as,

\[ -\frac{d[M]}{dt} = k_{tr,S}[S][M^*] \]  

Equation 8.22

In which, \( k_{tr,S} \) is the chain transferring constant to solvent molecules, and \([S]\) is the residual solvent concentration. Similar equations can be written for other transferring reactions to photoinitiators and monomers.
The overall polymerization degree of a free radical polymerization $X_n$ is a ratio of the chain propagation rate to the chain transferring rate.

\[
X_n = \frac{R_p}{R_i + k_{tr,S}[M^*][S] + k_{tr,PI}[M^*][PI] + k_{tr,M}[M^*][M]}
\] 8.23

Where, $k_{tr,PI}$ and $k_{tr,M}$ are the reaction constants of chain transferring to the photoinitiators and to the monomers respectively.

### 8.2.3 Termination

In general, the UV polymerization is mainly terminated by conventional coupling or disproportionation; however, it could be terminated by oxygen inhibition and could also be affected by the catalytic effect of metal oxide nanoparticles.

#### 8.2.3.1 Coupling or disproportionation

After initiation, the termination reactions start by two free radicals react together to neutralize the free radical activation centers by either coupling or disproportionation mechanisms.

\[
M_m^\ast + M_n^\ast \xrightarrow{k_{\text{sc}}} P_{m+n}
\] 8.24

\[
M_m^\ast + M_n^\ast \xrightarrow{k_{\text{sd}}} P_m + P_n
\] 8.25

\[
- \frac{d[M^\ast]}{dt} = k_t[M^\ast]^2
\] 8.26

Where, $k_{\text{sc}}$ and $k_{\text{sd}}$ are the coupling and disproportionation reaction constants respectively, $k_t$ is the termination reaction constant combining both the coupling and disproportionation reactions.
8.2.3.2 Oxygen inhibition

\[ M^* + O_2 \rightarrow ROO^* \]  \hspace{1cm} 8.27

\[-\frac{d[M^*]}{dt} = k_{O_2}[M^*][O_2] \]  \hspace{1cm} 8.28

Where, \( k_{O_2} \) is the oxygen inhibition reaction constant.

8.2.3.3 Metal oxide nanoparticles

It is unknown that metal oxide nanoparticles may trap the free radicals or be catalytic to generate more free radicals. This reaction might be placed in the initiation list.

\[ \pm \frac{d[M^*]}{dt} = k_{MO}[M^*]^n[MO]^n \]  \hspace{1cm} 8.29

In which, \( k_{MO} \) is the metal oxide nanoparticle catalytic constant

Combining all above factors that may affect the termination, the overall termination rate is,

\[ \left[ -\frac{d[M^*]}{dt} \right]_{\text{overall}} = \left[ -\frac{d[M^*]}{dt} \right]_{k_i} + \left[ -\frac{d[M^*]}{dt} \right]_{O_2} + \left[ \pm \frac{d[M^*]}{dt} \right]_{MO} \]  \hspace{1cm} 8.30

If the quasi-steady state assumption (QSSA) applies, then the sum of the termination and initiation rates is zero, leading to a polynomial equation for \( [M^*] \). This could be solved and used as the estimate for the free radical concentration at each time step.

The expected modeling results are: (1) the monomer’s conversion rate, (2) the photoinitiator’s consumption rate, (3) the temperature profile (1-3 varying with time and locations in the film) and (4) the linkage of the polymerization conditions to the mechanical properties. Based on these results, the optimal formulation and the polymerization conditions can be developed.

8.3 Modeling parameters

As a preliminary study, the values of UV polymerization parameters for modeling could be estimated from the literature (Decker and Jenkins 1985; Xu, Asghar et al. 1990; Decker 1992) (Skeirik and Gruulke 1986), the Polymer Handbook (Brandrup, Immergut et
Considering a 100 nm SR399/Irgacure184 coating under UV radiation (440mW/cm²) in CO₂ as a simple model system, and assuming the UV polymerization are initiated by UV factor only and the termination is only by coupling or disproportionation (no free radical transfers), applying the differential equations in above discussions and the estimated parameters in Table 8.1, we wrote a simple program with the software Maple 9.5 to do some computer modeling study. Some preliminary results—such as the [C=C] conversion rate, the photoinitiator decomposition rate and the free radical concentration—were obtained and plotted in Figure 8.4 and Figure 8.5. The FTIR measured [C=C] concentration is the average value across the coating, while the modeling results are the values at the middle of the coatings. An example of Map 9.5 codes for the kinetic modeling study is attached in the Appendix C.

In Figure 8.4, the measured data of the [C=C] conversion are in the red solid diamond points, and the initial modeling results are in the thin solid blue line (using the estimated values of $k_{d,pt} = 0.3757 \frac{1}{s}$ and $k_p = 5,000 \frac{\text{liter}}{mol \times s}$ from Table 8.1). Since this model system has no metal oxide nanoparticles, we approximated the value of $k_{d,pt}$ as a constant across the 100 nm thickness coating. It is apparent that the model predicts the trend well, except for some differences existing at the initial polymerization stage. It is interesting to find that one of the model results, presented as a heavy solid coffee-color line in Figure 8.4, fits the experimental data perfectly if the value of the photoinitiator’s dissociation constant $k_{d,pt}$ increases as a factor of three and the propagation constant $k_p$ increases as a factor of two as the initial estimated values in Table 8.1, which is absolutely possible for an UV polymerization. That is, $(4 k_{d,pt}, 2 k_p)$ seems the more reasonable estimated parameter’s values to the experiment. Correspondingly, the photoinitiator’s concentration and the free radical concentration profiles at the middle of the coating ($Z = 50nm$) are predicted by the model in Figure 8.5.
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<tr>
<td>SR399</td>
<td>the rate constant of the radical scavenged by (O_2) molecules, (k_o)</td>
<td>(-5E+8)</td>
<td>L⁺mol⁻¹s⁻¹</td>
<td></td>
<td>(Decker, 1985)</td>
</tr>
<tr>
<td>SR399</td>
<td>the saturated concentration of dissolved (O_2)</td>
<td>(-1E-3)</td>
<td>mol*L⁻¹</td>
<td></td>
<td>(Decker, 1985)</td>
</tr>
<tr>
<td>Irgacure 184</td>
<td>Molecular weight</td>
<td>204.3</td>
<td>g/mol</td>
<td></td>
<td>Ciba-Geigy</td>
</tr>
<tr>
<td>Irgacure 184</td>
<td>density, (\rho)</td>
<td>1.08</td>
<td>g/cm³</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Irgacure 184</td>
<td>extinction coefficient, (\varepsilon)</td>
<td>940</td>
<td>m²/mol</td>
<td></td>
<td>measured by UV-Vis</td>
</tr>
<tr>
<td>Irgacure 184</td>
<td>dissociation constant (k_{d,PI})</td>
<td>0.0044Iₜe⁻¹ at((H) - Z)</td>
<td>+ 0.0018</td>
<td>(\psi = \varepsilon_{\text{MO}} + \varepsilon_{\text{PI}} + \varepsilon_{\text{M}})</td>
<td>(Decker, 1992)</td>
</tr>
<tr>
<td>CeO₂</td>
<td>Molecular weight</td>
<td>172.1</td>
<td>g/mol</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CeO₂</td>
<td>density, (\rho)</td>
<td>7.7</td>
<td>g/cm³</td>
<td>10.17g/cm³</td>
<td></td>
</tr>
<tr>
<td>CeO₂</td>
<td>heat capacity, (C_p)</td>
<td>55252</td>
<td>J/kmol*K</td>
<td>25°C</td>
<td>Taken as TiO₂</td>
</tr>
<tr>
<td>CeO₂</td>
<td>heat conductivity, (k)</td>
<td>6.69</td>
<td>W/m*K</td>
<td>100°C</td>
<td></td>
</tr>
<tr>
<td>CeO₂</td>
<td>extinction coefficient, (\varepsilon)</td>
<td>365</td>
<td>m²/mol</td>
<td></td>
<td>measured by UV-Vis</td>
</tr>
<tr>
<td>TiO₂</td>
<td>Molecular weight</td>
<td>79.9</td>
<td>kg/kmol</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TiO₂</td>
<td>density, (\rho)</td>
<td>3.9</td>
<td>g/cm³</td>
<td>25°C</td>
<td></td>
</tr>
<tr>
<td>TiO₂</td>
<td>heat capacity, (C_p)</td>
<td>0.17</td>
<td>cal/g*K</td>
<td>25°C</td>
<td></td>
</tr>
<tr>
<td>TiO₂</td>
<td>heat capacity, (C_p) @ 25°C</td>
<td>55252</td>
<td>J/kmol*K</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TiO₂</td>
<td>heat capacity, (C_p) @ 40°C</td>
<td>56714</td>
<td>J/kmol*K</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TiO₂</td>
<td>heat capacity, (C_p) @ 60°C</td>
<td>58478</td>
<td>J/kmol*K</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TiO₂</td>
<td>heat conductivity, (k)</td>
<td>6.69</td>
<td>W/m*K</td>
<td>100°C</td>
<td></td>
</tr>
<tr>
<td>TiO₂</td>
<td>extinction coefficient, (\varepsilon)</td>
<td>795</td>
<td>m²/mol</td>
<td></td>
<td>measured by UV-Vis</td>
</tr>
<tr>
<td>O₂</td>
<td>concentration in air</td>
<td>0.009</td>
<td>mol/liter</td>
<td>1 atm</td>
<td>0.2/22.4</td>
</tr>
<tr>
<td>O₂</td>
<td>Diffusion in PMMA</td>
<td>3.80E+03</td>
<td>cm²/s⁻¹</td>
<td>1 bar, 20°C</td>
<td>(Brandrup, 1999)</td>
</tr>
<tr>
<td>O₂</td>
<td>Diffusion in PMMA</td>
<td>1.40E+04</td>
<td>cm²/s⁻¹</td>
<td>2 bar, 20°C</td>
<td>(Brandrup, 1999)</td>
</tr>
<tr>
<td>O₂</td>
<td>diffusion in monomers, (D_{O_2})</td>
<td>1.00E-06</td>
<td>cm²/s⁻¹</td>
<td>25-30°C</td>
<td>(Brandrup, 1999)</td>
</tr>
<tr>
<td>O₂</td>
<td>diffusion in polymers, (D_{O_2})</td>
<td>1.00E-08</td>
<td>cm²/s⁻¹</td>
<td>25-30°C</td>
<td>(Brandrup, 1999)</td>
</tr>
<tr>
<td>O₂</td>
<td>inhibiting constant in MMA, (k_{O_2})</td>
<td>1.00E+07</td>
<td>liter/(mol*s)</td>
<td>50°C</td>
<td>(Gruulke, 1994)</td>
</tr>
</tbody>
</table>
A rich amount of valuable information can be obtained from these modeling results. For example, the maximum conversion of [C=C] could be further increased, such as the case of the dotted green line in Figure 8.4 ($2k_{d,p}, 2k_p$), if ideally keeping the propagation rate, while reducing in half the photoinitiator’s dissociation rate. This means that the photoinitiator’s dissociation rate needs to be slowed down in order to provide free radicals in the system for a longer period to allow the chain propagations. This could be achieved by choosing a less active photoinitiator, or alternatively by reducing the UV intensity. If the photoinitiator’s activity is further reduced, such as the case of the dotted purple line ($k_{d,p}, 2k_p$), then the less amount of free radicals generated in a unit time is a bottle-neck for the polymerization, resulting in a lower maximum [C=C] conversion.

In order to apply the established models appropriately, accurate and direct measurements for the parameters are critical in the future. However, some of them are not easily obtained and require sophisticated instruments. From literature study, the methods to obtain these parameters are listed in Table 8.2. For example, the UV light intensity and the extinction coefficients of materials can be measured by an UV-Vis spectrometer, the [C=C] conversion rate can be measured by a real-time FTIR and the free radical concentration [$M^*$] can be monitored by a electron paramagnetic resonance spectroscopy (EPR), then the polymerization constants, such as the initiation constant, the propagation constant, the termination constant and the photoinitiator’s dissociation constant, can be derived based on the principle UV polymerization mechanisms.
Figure 8-4  The [C=C] depletion rate in a 100 nm SR399/184 coating.
Figure 8-5  The modeling data of photoinitiator’s depletion [PI] and free radical concentration [M*] in the middle of a 100 nm coating
Table 8-2 The methods to measure the parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>How to measure</th>
<th>Where/literature</th>
</tr>
</thead>
<tbody>
<tr>
<td>UV light profile, $I_0$</td>
<td>Thad, Charles</td>
<td>ODC</td>
</tr>
<tr>
<td>Extinction coefficient of each component in composition, $\varepsilon$</td>
<td>$A = -\ln \frac{I}{I_0} = \varepsilon[C]b$</td>
<td>ODC</td>
</tr>
<tr>
<td>Photoinitiator dissociation constant ( $k_d$ ) or life-time ($\xi$)</td>
<td>UV spectrometer. $\ln \frac{[PI]}{[PI]_0} = -k_d t$</td>
<td>TBD/Ciba-Geigy</td>
</tr>
<tr>
<td>Active energy of initiator dissociation by heat, $E_d$</td>
<td>From Arrhenius equation, $\ln k_d = \ln A - E_d / RT$ Plot $\ln k_d$ vs $1/RT$, the slop is $E_d$</td>
<td>TBD/Ciba-Geigy</td>
</tr>
<tr>
<td>Initiation rate, $R_i$</td>
<td>Measure the inducing time for polymerizations (real-time FTIR) by adding a known amount of high efficient inhibitor (free radical killers). $R_i = \frac{n[Z]_0}{t}$</td>
<td>ODC/UK</td>
</tr>
<tr>
<td>Efficiency of initiation, $\phi$</td>
<td>$\phi = \frac{R_i}{2k_d [PI]_0}$ based on above measurements</td>
<td>UK</td>
</tr>
<tr>
<td>Propagation constant, $k_p$</td>
<td>Real-time FTIR study.</td>
<td>ODC/UK</td>
</tr>
<tr>
<td>Termination constant, $k_t$</td>
<td>$\frac{k_p^2}{k_i} = \frac{2R_p^2}{R_i[M]^2} = \frac{2R_p V}{[M]^2}$, $\tau = \frac{k_p[M]}{2k_i R_p} = \frac{k_p}{k_i}$, $\Delta[M]_0 = \frac{k_p}{2k_i} \ln \cosh \left( \frac{t}{\tau} \right) = \frac{k_p}{2\tau k_i} (t - \tau \ln 2)$ at ($t \gg \tau$)</td>
<td>(Decker 1992)</td>
</tr>
<tr>
<td>Free radical life-time, $\tau$</td>
<td>Electron paramagnetic resonance spectroscopy (EPR) to measure $[M^*]$ for $k_p$</td>
<td>Carswell, 1990</td>
</tr>
</tbody>
</table>

$k_i$ M.Buback, 1992
Chain transfer constant, 

\[ C_M = \frac{k_{tr,M}}{k_p} \]

\[ C_{PI} = \frac{k_{tr,PI}}{k_p} \]

\[ C_S = \frac{k_{tr,s}}{k_p} \]

\[
\left( \frac{1}{X_n} - \frac{2k_{\ell}}{k_p} \right) \left( \frac{R_p}{[M]^2} \right) = C_M + C_I \frac{[PI]}{[M]}
\]

Plot left term vs \([PI]/[M]\).

**8.4 Summary**

It is of academic and practical interest to further study some areas in the future, including the kinetics of UV polymerization. Preliminary experimental results show that UV polymerizations are significantly affected by monomer type and functionality, photoinitiator type and amount, UV source, metal oxide nanoparticles inside, residual solvents and environmental gases. To model the UV polymerization process, with the consideration of all these factors, by a fundamental, mechanism-based approach is an efficient way to study a complicated reaction and save money. The results from modeling examined by the experiments, such as the photoinitiator dissociation and the \([C=C]\) concentration reduction profiles changing with time and location, help to identify the rate limiting steps and how these vary during polymerization. Optimization of the coating formulation and the UV polymerization conditions can follow. However, the direct and accurate measurements for the polymerization parameters are critical and requiring time and sophisticated instruments, the tasks are subjected to the future work. Maple 9.5, Fluent and Femlab could be used as the modeling software.

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Chapter Nine : Conclusion

This new approach to fabricating anti-reflective coatings and scratching resistant coatings by an in mold spin-coating process is very promising and demonstrates the advantages of this method over the traditional vacuum deposition ceramic coatings when using plastic substrates. This method developed as a part of content has been applied for an US patent (Application # 20060065989) by Optical Dynamics Corporation. In June 2006, the developed product, nanoCLEAR® AR lenses of Optical Dynamics Corporation, has been chosen as one of the 50 winners of the second annual Nano 50™ Awards by Nanotech Briefs®. According to Nanotech Briefs®, “this product was recognized as one of the top 50 technologies, products, and innovators that have significantly impacted - or are expected to impact - the state of the art in nanotechnology.” This achievement was made based on the numerous efforts of the research team and significant progress in technology developments. The work of this dissertation, mainly applying nanoindentation and nanoscratch techniques to directly measure the mechanical properties of as-produced multilayer nanocomposite coatings, has greatly accelerated ODC’s coating development, materials selection and structural design processes.

Nanoindentation tests have proven powerful for their capability to obtain various mechanical properties such as elastic modulus, hardness, residual stress, adhesion, and coating fracture toughness of the ultrathin polymeric nanocomposite coatings. The testing results such as elastic modulus are affected by the type of the substrate, thickness of the coating, residual stresses and the material nature.

9.1 The effect of polymer viscoelasticity on test methods

Because of the viscoelastic nature of polymer materials, viscous flow occurs during constant load indentation. The effect of viscous flow on the unloading behavior could be evaluated by indentation tests in which a constant indentation load was maintained for different holding times between the end of the loading phase and the start of the unloading phase. It was found that the reduced contact modulus obtained from the unloading curves decreased as the holding time increased and converged to a relatively constant value of 4.78 GPa for holding times greater than 2 seconds. This
effect is interpreted as an elastic rebound when the indenter load is removed before a quasi steady-state polymer flow is achieved. A critical holding time exists for the specific polymer where, for times exceeding a critical holding time, the dynamic effect is negligible.

The viscous flow itself could be quantitatively characterized by the time dependence of the indentation depth for the indentations on an ultrathin polymeric coating at a constant indentation load. The indentation depth between the end of the loading phase and the start of the unloading phase is a linear function of the holding time. That is, the indentation velocity is independent of the indentation stress even though the indentation stress decreases with the increase of the indentation depth. This fact suggests that the flow behavior of the ultrathin polymer coating is shear-thinning. For the flow behavior of the SR399 ultrathin coatings, there is a relation between the indentation depth and time with the stress exponent being $\frac{1}{2}$.

**9.2 The substrate effect**

**9.2.1 Stiff substrates**

The 10% rule of thumb is still valid for a submicron polymeric coating on a stiff substrate; that is, the intrinsic elastic modulus of a coating can be estimated when the indentation penetration depth is less than 10% of the coating thickness. No scaling effect was observed on the behavior of surface elasticity for the ultrathin polymeric films.

At larger indentation loads or deeper indentation depths, the reduced contact modulus increased with the indentation load due to the effect of a stiff substrate. The effect of substrate on the reduced contact modulus can be described by an elastic contact model for the indentations with a larger contact radius than the film thickness. Quantitative agreement between the model and the experimental results is obtained.

**9.2.2 Compliant substrates**

The same polymeric coatings used for the stiff substrate studies were spin-coated on compliant substrates. The overall elastic response from the experiments indicated that the ratio of the elastic modulus between the coating and the substrate, the indenter tip size, the coating thickness, the adhesion property and residual stress influenced the
effective modulus of the coating-substrate system in a complex way. However, the effective modulus of the coating-substrate system is logarithmic dependence on the ratio of the indentation depth to the coating thickness, before any fracture of the coatings occurs.

Three potential models have been examined to extract intrinsic elastic modulus of a relatively stiff polymeric coating from the influence of a compliant substrate. The Hsueh’s elastic model can fit the experimental data fairly well as long as the indenter tip retains its spherical geometry. In order to validate the Gao’s model for submicron polymeric coatings, the residual stress effects of the coatings and the interface between the coating and the substrate need to be taken into account. Although the Korsunsky’s model fitted surprisingly well for submicron meter coatings, the theoretical bases are subject to further investigation. Overall, a more applicable model needs to be developed in the future for interpreting the elastic response of a stiff coating on a compliant substrate.

9.3 Interfacial adhesion strength

Indentation-induced delamination provides a unique approach to evaluate the interfacial strength between a surface coating and a compliant substrate. Assuming that the contact radius is much larger than the thickness of the surface coating, the deformation behavior of the thin surface coating could be approximated as a plane-stress like state. Using a shear-lag model, we have established a relationship between the critical indentation load and the interfacial strength at which interfacial delamination initiates. The ratio of the critical indentation load to the cube of the corresponding indentation depth turns out to be a linear function of the reciprocal of the coating thickness.

The analysis above was verified by the experimental indentation-induced delamination of crosslinked polymer ultrathin surface coatings over an acrylic substrate. For the submicron coatings, only one excursion phenomenon is observed in the loading phase, suggesting that the interfacial crack is arrested for deep indentations. The dependence of the critical indentation load on the coating thickness agrees with the proposed model. The interfacial strength is found to be 70.35 MPa (the coating modulus:
5.13 GPa and the acrylic plate: 2.74 GPa Differing from the indentation behavior of the submicron coatings, the micron scale polymeric coating displays multiple excursions in the loading curve. This is due to the arrest of interfacial cracks during the indentation and the increase of the radial stress with further indentation. Once the radial stress reaches the interfacial strength, the interfacial delamination is initiated again. It should be pointed out that a new model is needed for evaluating the indentation-induced delamination in thick coatings, which may require the use of numerical simulation.

9.4 Fracture phenomena of AR coatings

The mechanical response of a nanocomposite AR lens by a newer technology has been compared with a ceramic AR lens by a well established technology. This analysis was focus on the common surface failure phenomena under indentation and scratching stresses. It is proven that the spin-coated nanocomposite AR coatings have a stronger damage resistance than the traditional ceramic AR coatings. The failures, including: scratching, delamination and crazing (commonly occurring with rapid strain fluctuations), led to light scattering that reduces the optical efficiencies of the thin film filters. Ceramic film failures created a rougher surface damage that should led to more haze. The newer technology reported in this dissertation is designed to more closely match the elastic properties of the substrate, thus eliminating many of these issues and minimizing damage done to the final article.

9.5 UV polymerization for nanocomposite coatings

These polymeric nanocomposite coatings for AR lenses were fabricated by UV polymerization. The formulations and the processing conditions were optimized in order to balance the mechanical properties and adhesion strength, besides the optical performance, through the evaluation of nanoindentation and nanoscratching tests combining the FTIR studies. This study showed that the UV polymerization could be significantly affected by oxygen inhibition, transitional metal oxide nanoparticles and coating thickness.

In the presence of oxygen, the UV polymerization rate is retarded and the maximum polymerization degree is reduced due to the oxygen inhibition effect; that is,
the active free radicals react with oxygen molecules to form less active free radicals. Also, for the same reason, the maximum UV polymerization rate is lower at the normal polymerization period of an AR coating process.

Transitional metal oxide nanoparticles significantly absorb UV light at a wavelength less than 300 nm. Thus, the polymerization process with those photoinitiators, such as 1-hydroxy cyclohexyl phenyl ketone, whose dissociation is efficient at the wavelength of 256 nm, is retarded considerably. Within the normal polymerization time for these coatings, the maximum polymerization rate is also reduced. It is predictable that the UV intensity at the top surface of the coating is much stronger than that at the bottom of the coating, and there is likely a gradient in conversion across the coating thickness.

The coating thickness also affects the UV polymerization. In the presence of oxygen, a thinner coating presents a lower polymerization degree because oxygen molecules diffuse into the coating more easily. However, the metal oxide nanoparticles absorb UV light more than a thinner coating thus retarding the polymerization rate, reducing the conversion and likely forming a conversion gradient across the film.
# Appendix A: Nomenclature

<table>
<thead>
<tr>
<th><strong>Symbol</strong></th>
<th><strong>Description</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>$A$</td>
<td>Indentation contact Area between indenter and material</td>
</tr>
<tr>
<td></td>
<td>UV light absorption</td>
</tr>
<tr>
<td>$A_r$</td>
<td>projected contact area between material and indenter in direction of scratching</td>
</tr>
<tr>
<td>$a$</td>
<td>contact radius of contact area between indenter and material</td>
</tr>
<tr>
<td>$b$</td>
<td>Path-length of UV light</td>
</tr>
<tr>
<td>$c$</td>
<td>mole concentration</td>
</tr>
<tr>
<td>$C_p$</td>
<td>specific heat capacity</td>
</tr>
<tr>
<td>$C_c$</td>
<td>contact compliance</td>
</tr>
<tr>
<td>$C_m$</td>
<td>instrument compliance</td>
</tr>
<tr>
<td>$E_r$</td>
<td>reduced elastic modulus</td>
</tr>
<tr>
<td>$E_i$</td>
<td>elastic modulus of indenter</td>
</tr>
<tr>
<td>$E_s$</td>
<td>elastic modulus of indented material or modulus of substrate</td>
</tr>
<tr>
<td>$E_c$</td>
<td>elastic modulus of coating</td>
</tr>
<tr>
<td>$E^*$</td>
<td>apparent (composite/effective) modulus of coating-substrate system</td>
</tr>
<tr>
<td>(\tilde{E}_r)</td>
<td>the reduced contact modulus using contact area for indentation of an elastic half-space by a conical indenter in Eq. 4.6</td>
</tr>
<tr>
<td>$F$</td>
<td>Indentation (maximum) load</td>
</tr>
<tr>
<td>$F^*$</td>
<td>critical load at which crack initiates</td>
</tr>
<tr>
<td>$F_T$</td>
<td>tangential load resisting indenter moving in scratching direction</td>
</tr>
<tr>
<td>$f$</td>
<td>efficiency of a free radical initiating a polymerization</td>
</tr>
<tr>
<td>Symbol</td>
<td>Definition</td>
</tr>
<tr>
<td>--------</td>
<td>------------</td>
</tr>
<tr>
<td><strong>H</strong></td>
<td>Hardness</td>
</tr>
<tr>
<td>( H_{\text{sys}} )</td>
<td>effective hardness of a coating-substrate system</td>
</tr>
<tr>
<td>( H_N )</td>
<td>scratching normal hardness (dynamic hardness)</td>
</tr>
<tr>
<td>( H_T )</td>
<td>tangent hardness in scratching direction</td>
</tr>
<tr>
<td><strong>h</strong></td>
<td>coating thickness</td>
</tr>
<tr>
<td><strong>K_c</strong></td>
<td>fracture toughness</td>
</tr>
<tr>
<td>( \phi )</td>
<td>a parameter related to coating fracture in Eq. 3.16</td>
</tr>
<tr>
<td>( \theta )</td>
<td>the half included angle of indenter</td>
</tr>
<tr>
<td><strong>h</strong></td>
<td>heat transfer coefficient</td>
</tr>
<tr>
<td><strong>I</strong></td>
<td>transmitted light intensity</td>
</tr>
<tr>
<td>( I_0 )</td>
<td>incident light intensity</td>
</tr>
<tr>
<td><strong>k</strong></td>
<td>thermal conductivity</td>
</tr>
<tr>
<td>( k )</td>
<td>a constant (for ( n = 1 ), ( k ) is the viscosity) in Eq. 4.7</td>
</tr>
<tr>
<td>( k_p )</td>
<td>chain propagation constant</td>
</tr>
<tr>
<td>( k_{d,\text{PI}} )</td>
<td>dissociation constant of photoinitiator</td>
</tr>
<tr>
<td>( k_t )</td>
<td>termination constant</td>
</tr>
<tr>
<td>( k_{p,\lambda-\text{noPI}} )</td>
<td>propagation constant of UV polymerization without photoinitiators</td>
</tr>
<tr>
<td>( k_{i,\lambda-\text{noPI}} )</td>
<td>initiation constant of UV polymerization without photoinitiators</td>
</tr>
<tr>
<td>( k_{t,\lambda-\text{noPI}} )</td>
<td>termination constant of UV polymerization without photoinitiators</td>
</tr>
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<td>( k_{r,S} )</td>
<td>chain transferring constant to solvent molecules</td>
</tr>
<tr>
<td>( k_{r,\text{PI}} )</td>
<td>chain transferring constant to photoinitiator</td>
</tr>
<tr>
<td>Symbol</td>
<td>Description</td>
</tr>
<tr>
<td>--------</td>
<td>--------------------------------------------------</td>
</tr>
<tr>
<td>$k_{tr,M}$</td>
<td>chain transferring constant to monomer</td>
</tr>
<tr>
<td>$k_{O_2}$</td>
<td>oxygen inhibition constant</td>
</tr>
<tr>
<td>$k_{tc}$</td>
<td>coupling termination constant</td>
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<tr>
<td>$k_{td}$</td>
<td>disproportionation termination constant</td>
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<tr>
<td>$M^*$</td>
<td>molecular free radical</td>
</tr>
<tr>
<td>$n$</td>
<td>stress exponent in Eq. 4.7</td>
</tr>
<tr>
<td>$R$</td>
<td>Indenter tip radius</td>
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<td>free radical of photoiniator</td>
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<td>$R_i$</td>
<td>Initiation rate</td>
</tr>
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<td>$R_p$</td>
<td>propagation constant / chain growth constant</td>
</tr>
<tr>
<td>$S$</td>
<td>unloading stiffness</td>
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<tr>
<td>$t$</td>
<td>time</td>
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<td>coating thickness in Eq. 3.6</td>
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<td>$X_n$</td>
<td>polymerization degree</td>
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<tr>
<td>$Y$</td>
<td>yield strength</td>
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<tr>
<td>$\mu$</td>
<td>shear modulus</td>
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<td>$\beta$</td>
<td>a constant related to coating thickness in Eq. 3.6</td>
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<td>Symbol</td>
<td>Definition</td>
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<td>------------</td>
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<tr>
<td>$\tau$</td>
<td>shear stress</td>
</tr>
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<td>$\tau$</td>
<td>free radical life-time</td>
</tr>
<tr>
<td>$\tau_m$</td>
<td>maximum interfacial stress</td>
</tr>
<tr>
<td>$\tau_{cr}$</td>
<td>critical interfacial shear strength at which delamination occurs</td>
</tr>
<tr>
<td>$\dot{\gamma}$</td>
<td>shear rate</td>
</tr>
<tr>
<td>$\Gamma$</td>
<td>fracture energy</td>
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<tr>
<td>$\rho$</td>
<td>density</td>
</tr>
<tr>
<td>$\delta$</td>
<td>indenter penetration depth</td>
</tr>
<tr>
<td>$\delta_c$</td>
<td>indentation contact area between an indenter and material surface</td>
</tr>
<tr>
<td>$\delta_{\text{max}}$</td>
<td>maximum indentation depth</td>
</tr>
<tr>
<td>$\delta_{\infty}$</td>
<td>Indentation depth in an Infinite thick coating</td>
</tr>
<tr>
<td>$\delta_e$</td>
<td>elastic indentation depth</td>
</tr>
<tr>
<td>$\delta_p$</td>
<td>plastic indentation depth</td>
</tr>
<tr>
<td>$\delta_{\text{creep}}$</td>
<td>creep indentation depth</td>
</tr>
<tr>
<td>$\nu_i$</td>
<td>Poisson’s ratio of the indenter</td>
</tr>
<tr>
<td>$\nu_s$</td>
<td>Poisson’s ration of indented material</td>
</tr>
<tr>
<td>$\nu_c$</td>
<td>coating’s Poisson ratio</td>
</tr>
<tr>
<td>$\phi$</td>
<td>volume fraction of particle</td>
</tr>
<tr>
<td>$\phi_i$</td>
<td>quantum yield of photoinitiator dissociation efficiency under UV radiation</td>
</tr>
<tr>
<td>$\phi_{DN}$</td>
<td>weight function in Eq. 3.5</td>
</tr>
<tr>
<td>$\phi_m$</td>
<td>maximum packing fraction</td>
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<tr>
<td>$\tau$</td>
<td>stress</td>
</tr>
<tr>
<td>$\varepsilon$</td>
<td>extinction coefficient</td>
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**Subscript:**

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<th>Subscript</th>
<th>Description</th>
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<td>coating</td>
</tr>
<tr>
<td>$eff$</td>
<td>overall “effective” response of a coating-substrate system during indentation</td>
</tr>
<tr>
<td>$s$</td>
<td>substrate</td>
</tr>
<tr>
<td>$M$</td>
<td>monomer</td>
</tr>
<tr>
<td>$MO$</td>
<td>metal oxide</td>
</tr>
<tr>
<td>$PI$</td>
<td>photoinitiator</td>
</tr>
<tr>
<td>$0$</td>
<td>initial status</td>
</tr>
<tr>
<td>$t$</td>
<td>status at time $t$</td>
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</table>
Appendix B: Calibration procedures of nanoindentation instrument

B1. The instrument load frame compliance

Specimen: Fused quartz from Hysitron

**Experiment procedure**

1. Set up the instrument parameters.
   
   Note: the machine compliance was set as 0.

2. A series of indentation tests with load from 100 μN to 4,000 μN:
   
   The testing conditions are loading for 10 seconds and unloading for 10 seconds linearly, no holding time was applied.
(3) Calculate the machine compliance $C_m$ using Equation 3.27.

The intercept: $C_m = 0.0008 \text{ nm/} \mu \text{N} = 0.8 \text{ nm/} \mu \text{N}$

(4) Fill in the calibrated machine compliance in the parameter setting
Note

Talked with the technical support of Hysitron, Mr.Lance Kuhn, who calibrated our instrument in June, 2002, said the typical machine compliance for this type of D1 transducer is in the range of 0.0007 to 0.001 nm/\(\mu\)N, varying with the installation of the indenter and the environmental temperature.

The Berkovich tip is more ideal for this characterization of the load-frame compliance than a cubic corner, because a sharper indenter could cause cracks with quartz at a very high indentation load, giving a wrong machine compliance data.

Using magnetic plate to fix the quartz sample is recommended. The testing conditions and the tip requirement were not stated in the menu.
**B2 Tip Area Function**

The general format of a tip area function is:

\[ A(h_c) = C_0 h_c^2 + C_1 h_c + C_2 h_c^{1/2} + C_3 h_c^{1/4} + C_4 h_c^{1/8} + C_5 h_c^{1/16} \]

**Experiment procedure**

1. Using “Advanced Z-axis calibration” in the menu of file: set the parameters as below.

2. Calculate the Tip Area Function from the data of the moduli tested on a quartz sample. The value of \( C_0 \) can be set at 2.598 as an ideal cubic corner (Figure a), or to select the “vary \( C_0 \)” for a better mathematic fitting (Figure b). It is recommended to vary \( C_0 \) for the study at the range of small penetration depths.
(3) Double check the measuring results by using the calculated TAF

(a) On the standard quartz sample (Er 69.6 GPa, H 9.5-9.7 GPa)
(b) On a PMMA standard sample from Hysitron (Er 5.5~5.9GPa, H ? )
(The same test was conducted two times at the different days: one is in red squares and another is in blue crosses)
**B3: Calibration of transducer**

**B3a: 1D transducer**

The following calibration is for Z-calibration in the vertical direction.

(2) Check the parameters of the Transducer Zero-volt gap and its Zero-volt ESF as the values shown below. Normally keep the manual bias-offset at 0.2.

(3) Click the “Calibration Transducer” and check the initial parameters.
(4) Adjust the “Zero” course and fine knobs to 0 as close as possible.

(5) Re-adjust the “Zero” course and fine knobs to 0 as close as possible.
(6) The instrument calculates the parameters

(7) The result displacement
B3b: 2D transducer

The calibration of a 2D transducer contains a vertical Z-calibration and a lateral X-calibration. The following procedure is for X-calibration only, such as the parameters of the force constant and plate spacing, etc.

*Extremely important:* the calibration is conducted with the tip in the air.

**Experiment procedure**

(1) Load the standard calibration load function from the path of:

c:\program files\triboscope41FB\loadfunctions\x_axis_calibration_scratch.scf
(2) Select the “drift correction” from the setup menu

(3) Save as an “air” calibration file
(4) The result from self-testing.

Note: the lateral force is normally not zero, which should be as close to zero as possible.

(5) To set the lateral force close to Zero, click the “calibrate” from the file menu.
(6) After clicking the calibrate, the lateral force is close to zero, meanwhile, the normal force and normal displacement should be close to zero as well.

If the lateral force is close to zero, the calibration is done.
Appendix C: Kinetics model program

In the following two examples, Maple 9.0 is the software used for the kinetics modeling study. The first example is the UV polymerization of SR399 monomers without containing any photoinitiators. And the second one is the UV polymerization of SR399 monomers initiated by Irgacure 184 photoinitiators. The possible mechanisms were discussed in Chapter Eight. The parameters applied in this sample modeling were estimated from literature.

C1: UV polymerization without photoinitiators

> restart;
> # free radical photopolymerization, thin films
> # the polymerization process is decomposed into individual initiation, propagation and termination mechanisms
> # Initiation
> # I1. UV initiation of methacrylate monomer
> # M = monomer, t=time, In= light intensity, R = chain radical, conc. in mol/m3
> C0:=11350;In0:=40;kp:=5.0;kt:=1.0e04;A:=4.16e-07;kdm:=kt*(A/kp)^2;

\[
\begin{align*}
C0 &:= 11350 \\
In0 &:= 40 \\
kp &:= 5.0000 \\
kt &:= 10000.0000 \\
A &:= 4.16e-07 \\
kdm &:= 6.922e11
\end{align*}
\]

> # initiation
> e1:=diff(Rm(t),t)=2*kdm*C(t)^2;

\[
eq1 := \frac{d}{dt} Rm(t) = 1.384 \times 10^{-10} C(t)^2
\]
\[ \text{ic1} := R_0 = 2 \times k_{\text{dm}} \times C_0; \]
\[ \text{ic1} := R_0 = 0.000015713 \]

# quasi steady state assumption
\[ R(t) = \sqrt{k_{\text{dm}}/k_t} \times C(t); \]
\[ R(t) = 8.320 \times 10^{-8} \times C(t) \]

# termination
\[ \text{eq2} := -\frac{d}{dt} R(t) = 2 \times k_t \times (k_{\text{dm}}/k_t) \times C(t)^2; \]
\[ \text{eq2} := -\frac{d}{dt} R(t) = 1.384 \times 10^{-10} \times C(t)^2 \]

# propagation
\[ \text{eq3} := -\frac{d}{dt} C(t) = k_p \times C(t) \times \sqrt{k_{\text{dm}}/k_t} \times C(t); \]
\[ \text{eq3} := -\frac{d}{dt} C(t) = 4.160 \times 10^{-7} \times C(t)^2 \]

\[ \text{ic2} := R(0) = 0.0; \]
\[ \text{ic2} := R(0) = 0.0000 \]

\[ \text{ic3} := C(0) = C_0; \]
\[ \text{ic3} := C(0) = 11350 \]

\[ \text{ans} := \text{dsolve}\{\text{eq1, eq2, eq3, ic1, ic2, ic3}\}, \{R(t), R(t), C(t)\}, \text{numeric}; \]
\[ \text{ans} := \text{proc}x_{\text{rk}45} \text{... end proc}; \]

\[ \text{ans}(15); \]
\[ [t = 15.0000, C(t) = 10599., R(t) = 0.24983, RT(t) = -0.24983] \]

\[ \text{tmax} := 1800.; \]
\[ \text{tmax} := 1800.0000 \]

\[ \text{with(plots)}; \]
Warning, the name changecoords has been redefined

# C(t) shows the change in C=C concentration with time
\[ \text{odeplot} \text{ans}, [t, C(t)], 0..\text{tmax}, \text{numpoints}=100); \]
C2: UV polymerization with photoinitiators

> restart;
> # free radical photopolymerization, thin films
> # the polymerization process is decomposed into individual
initiation, propagation and termination mechanisms
> # Initiation
> # I1. UV initiation of methacrylate monomer
> # M = monomer, t=time, In= light intensity, R = chain
radical, conc. in mol/m3
> C0:=11350; In0:=40.; kp:=5.0; kt:=1.0e04; A:=4.16e-
07; kdm:=kt*(A/kp)^2;

\[
C0 := 11350
\]

\[
In0 := 40.0000
\]
\[
kp := 5.0000 \\
kt := 10000.0000 \\
A := 4.160 \times 10^{-7} \\
kdm := 6.922 \times 10^{-11}
\]

> # initiation
> # UV initiation of monomer
\[
eq 1 := \text{diff}(\text{Rm}(t),t) = 2 \times kdm \times C(t)^2;
\]

\[
eq 1 := \frac{d}{dt} Rm(t) = 1.384 \times 10^{-10} C(t)^2
\]

> ic1 := Rm(0) = 8.32e-08 \times C0;

\[
ic1 := Rm(0) = 0.0011232
\]

> # UV initiation of photoinitiator
> # In is the light intensity (W/m2-s), f is the film factor, kint is from the paper, Photo0 is the initial photoinitiator concentration, a is the efficiency of the photoinit radical, 0 < a < 1.
\[
In := 100.; kint := 0.0004; f := 0.9393; Photo0 := 291.7; a := 0.3;
\]

\[
In := 100.0000 \\
kint := 0.00040000 \\
f := 0.93930 \\
Photo0 := 291.70 \\
a := 0.30000
\]

> # extinction coefficients. Ephoto is the photoinitiator value, Em is the monomer value, m2/mol
\[
Ephoto := 940; Em := 86.2;
\]

\[
Ephoto := 940 \\
Em := 86.200
\]

> kdi := kint * f;
\[
\text{\texttt{kdi := 0.00037572}}
\]

> # in example 2A, we assume that the photoinitiator dissociates,
> but only 30\% of radicals form chains. The photoinitiator is
> consumed at the expected rate, but the radical balances are less.
> \texttt{eq2:=-diff(Photo(t),t)=Photo(t)*In*kdi;} 

\[
\text{eq2 := } -\frac{d}{dt} \text{Photo}(t) = 0.037572 \text{Photo}(t)
\]

> \texttt{ic2:=Photo(0)=Photo0;} 

\[
ic2 := \text{Photo}(0) = 291.70
\]

> \texttt{eq3:=diff(Rph(t),t)=2*a*Photo(t)*In*kdi;} 

\[
eq 3 := \frac{d}{dt} \text{Rph}(t) = 0.022543 \text{Photo}(t)
\]

> \texttt{ic3:=Rph(0)=0.0;} 

\[
ic3 := \text{Rph}(0) = 0.0000
\]

> # termination
> \texttt{eq4:=-diff(Rt(t),t)=2*kt*R(t)^2;} 

\[
\text{eq4 := } -\frac{d}{dt} \text{Rt}(t) = 1.384 \times 10^{-10} \text{C}(t)^2 + 0.022543 \text{Photo}(t)
\]

> \texttt{ic4:=Rt(0)=0.0;} 

\[
ic4 := \text{Rt}(0) = 0.0000
\]

> # quasi steady state assumption

\[
\text{R}(t) := \sqrt{(kdm/kt) \times C(t)^2 + (kdi/kt) \times a \times In \times \text{Photo}(t)};
\]

\[
R(t) := \sqrt{6.922 \times 10^{-15} \text{C}(t)^2 + 0.0000011272 \text{Photo}(t)}
\]

> # propagation
> \texttt{eq5:=-diff(C(t),t)=kp*C(t)*R(t);} 

\[
eq 5 := -\frac{d}{dt} \text{C}(t) = 5.0000 \text{C}(t) \sqrt{6.922 \times 10^{-15} \text{C}(t)^2 + 0.0000011272 \text{Photo}(t)}
\]
\[ \text{ic5} := C(0) = \text{C0}; \]

\[ \text{ic5} := C(0) = 13500 \]

\[ \text{ans} := \text{dsolve}\{\text{eq1, eq2, eq3, eq4, eq5, ic1, ic2, ic3, ic4, ic5}\}, \{\text{Rm(t), Photo(t), Rph(t), Rt(t), C(t)}\}, \text{numeric}; \]

\[ \text{ans} := \text{proc(x rkf45) ... end proc;} \]

\[ \text{ans}(30); \]

\[ t = 30.0000, C(t) = 1685.8, \text{Photo}(t) = 94.497, Rm(t) = 0.15430, Rph(t) = 118.32, Rt(t) = -118.48 \]

\[ \text{tmax} := 90.0; \]

\[ \text{tmax} := 90.0000 \]

\[ \text{with(plots):} \]

\[ \# \text{ R(t) shows the change in the total free radical concentration with time} \]

\[ \text{odeplot(ans,}[t, R(t)],0..tmax, \text{numpoints=100}); \]

\[ \# \text{ Photo(t) shows the change in photoinitiator with time} \]

\[ \text{odeplot(ans,}[t, \text{Photo}(t)],0..tmax, \text{numpoints=100}); \]
# $C(t)$ shows the change in C=C concentration with time

> odeplot(ans, [t, C(t)], 0..tmax, numpoints=100);
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Society for Optical Engineering 4580 (Optoelectronics, Materials, and Devices for Communications): 103-111.


Vita

Kebin Geng was born on April 5, 1967, in Wuhu, Anhui, China. He attended Sichuan University in Chengdu, Sichuan, China, where he received his Bachelor’s degree in Plastic Engineering in July, 1989 and his Masters’ degree in Polymer Material Science and Engineering in July, 1992. After his graduation in China, he served in SINOPEC (Chinese Petrochemical), Shell Petrochemical and PolyOne. He began his Ph.D. study in the Materials Science and Engineering program at the University of Kentucky in August, 2002.

Publications: