MECHANICAL CHARACTERIZATION OF VISCOELASTIC-PLASTIC

SOFT MATTER USING NANOIDENTATION

Dissertation

zur

Erlangung des Grades

', Doktor-Ingenieurin'

Der Fakultät für Maschinenbau

der Ruhr-Universität Bochum

von

Keerthika Balasundaram

aus Coimbatore, India.

Bochum 2009
Dissertation eingereicht am: 26.11.2008

Tag der mündlichen Prüfung: 03.03.2009

Erster Referent: Prof. Dr. Gunther Eggeler

Zweiter Referent: Prof. Dr. Dierk Raabe
**ABSTRACT**

Nanoindentation tests are widely used in recent years to characterize the nanomechanical properties of various materials. The analysis method proposed by Oliver & Pharr (OP) is widely adopted. However, recent studies revealed that the mechanical properties of viscoelastic-plastic (polymeric) materials determined using the OP method does not lead to a correct evaluation of Young’s modulus. In particular, the estimated elastic modulus is several times larger than the correct one, thus challenging the possibility of a nanomechanical characterization of polymers. Viscoelasticity, pile-up, or adhesive forces is usually blamed for this failure. Based on the issues above, we further examine the applicability of the OP method for characterizing the nanomechanical properties of polymeric materials, placing special emphasis on the reduced (instantaneous) modulus. The effects of the plastic deformation and the time-dependent deformation behavior on the fundamental relations in the OP method are studied by using finite element analysis based on a viscoelastic-plastic model developed for polymers which yields an experimental protocol. To validate the developed procedure experiments are performed on four different polymers. Results from experiments shows that using the standard OP method, the instantaneous modulus of the materials can be reliably determined. We observed a depth dependence in the obtained modulus, and are related to the effects of adhesion. Theoretical analysis is performed which permits to estimate the lower limit of the indentation depth beyond which the adhesion effects on the OP method and indentation creep tests are small. The results can be directly used and it is not necessary to invoke different adhesive contact theories (Johnson–Kendall–Roberts, Derjaguin–Muller–Toporov, or Maugis–Dugdale model). The critical indentation depth obtained from the experiments are in good agreement with the theoretical predictions. We made efforts to extend our results to Berkovich indenters there were edge problem, and severe localization affecting the properties of soft matter, where every polymer showed its unique contact flow behaviour. Thus we conclude that a spherical indenter in conjunction with the developed procedure can be reliably used to determine the properties of soft matter, being aware of the critical indentation depth.
ACKNOWLEDGMENTS

Gratitude is the memory of the heart. - Jean Baptiste Massieu

The work described in this thesis was carried out at the Max-Planck-Institut für Eisenforschung GmbH, Düsseldorf (MPIE) in connection with ‘International Max-Planck Research School for Surface and Interface Engineering in Advanced Materials’ (IMPRS-SurMat) curriculum.

At first, I would like to thank my advisor, Prof. D. Raabe, for supporting me over years, and for giving me so much freedom to explore and discover the field of nanomechanics. His guidance and encouragement throughout the course of my studies without which, I would not have been able to produce this piece of work. I should appreciate his willingness and kindness for correcting my paper and thesis. He always was and he is a constant source of motivation, still there is a lot to learn from you Prof. Raabe.

I am grateful to Dr. Y. P. Cao, for hours of discussions, guidance, insight, and mentorship, both on this thesis project and in general. I thank for his enthusiasm about our work, and fought many battles on our behalf. I have learned tremendously from him. Thank you uncle Cao.

Special thanks to Prof. Dr.-Ing. G. Eggeler for serving on my thesis committee. I express my sincere gratitude for his willingness to help.

I wish to thank Prof. Dr. Martin Stratmann and Prof. Dr. Gunther Eggeler (Spokesmen-SurMat) for providing an opportunity to pursue my doctoral study in this Max-Planck Research School. This project was generously funded from IMPRS-SurMat and MPIE. Thanks to Dr. A. Büttner and Dr. R. Loschen (Administrative Director-SurMat) for their constant tracking through E-mail and personally for SurMat school’s events and updates. Special thanks to Dr. C. Somsen. He has been extremely helpful in the intial registration issues in the RUB (Ruhr University Bochum).

Hearty acknowledgments to Ms. H. Bögershausen and Mr. F. Herbert for helping in performing measurements with the Triboscope. They were willing and very able to seek the best possible advice if the solution to the problem lies outside the scope of their expertise. I would like to thank Dr. U. Hangen (Hysitron) for his kindness, and assisting me when there were critical experimental issues. I would like to acknowledge the help from Scientific Computing and Computational Services, MPIE Mr. A. Kuhl, Mr. B. Beckschäfer and Mr. Ron McCormack. I
appreciate the help from Mr. P. Ebbinghaus and Dr. X. Wang for introducing me to the AFM. Special thanks Ms. E.S. Müller-Lorenz for helping me in SEM.

I am extremely grateful to my colleagues in the Microstructure Physics and Metal Forming (MSU), MPIE and from SurMat for their enduring support throughout the course of my studies. Thanks to Dr. A. Bastos, and Dr. I. Gutierrez, for sharing the office and I appreciate their patience for my anonymous questions popping up between works. I would like to thank all my friends for coffee breaks and small chats, BBQ, and all the celebration for providing a welcome distraction from academics. Thanks to fellow MPIE members Mr. L. Tao, Ms. M. Calcagnotto, Dr. C. Herrera, Mr. E. Demir, Ms. N. Elhami, Ms. A. Khorashadizadeh, Mr. E. Torres, Mr. F. Hamou, Ms. J. Zuo, Mr. and Ms. Mardare, Dr. A. Counts, Dr. S. Nikolov, and Dr. H. Fabritius. I should say that I had loads of fun and great laughs in their friendly company. I am grateful to all the Indian friends in Germany. Special thanks to Dr. S. Swaminithan and Dr. L. Neelakantan for their initial and constant support.

I wish to thank all my friends from India Ms. Deepa, Mr. Abdul, Mr. Nagarajan, Ms. Vidya, Ms. Ananthi and Mr. Nivas for their moral support. I am grateful to acknowledge all the lectures and Prof. who helped me to grow up to this stage. Mr. Sathananthan, Dr. Amuda, Ms. A. Brinda, Dr. L. Senthilkumar, Prof. Dr. S. Jayakumar, Prof. Dr. C. K. Shashidharan Nair and Mr. K. Sivakumaran. I would like to address a special thanks to Prof. U.K Mudali who provided an opportunity in beginning my career as a researcher.

I fell that my living in a foreign country would never been complete without friends from my hostel (Kolping Haus). This hostel is a place of international cultural exchange provided me a chance to meet people almost from everywhere on earth. Living in such a place provoked a new dimension in my life.

Finally it’s a pleasure to thank my beloved parents and my brother for their everlasting love, motivation, support and encouragement. I would like to thank all my well wishers in Germany, and back at home expecting me with a doctor title. I was trying to be as accurate as possible, for any omissions or inaccuracies I apologise and leave behind a word filled with gratitude ‘Thank U’.
# TABLE OF CONTENTS

| ABSTRACT | 3 |
| ACKNOWLEDGEMENTS | 4 |
| TABLE OF CONTENTS | 6 |
| LIST OF SYMBOLS AND ABBREVIATIONS | 8 |

1. INTRODUCTION 10
   1.1. MOTIVATION 10
   1.2. NANOINDENTATION BACKGROUND 13
      1.2.1 REVIEW OF MATHEMATICAL MODELS 13
   1.3. ANALYSIS OF NANOINDENTATION DATA 15
      1.3.1 OLIVER AND PHARR (OP) METHOD 16
   1.4. SCOPE OF THIS THESIS 18
   REFERENCES 21

2. COMPUTATIONAL STUDIES 26
   2.1. INTRODUCTION 26
   2.2. COMPUTATIONAL MODELLING OF THE SPHERICAL INDENTATION INTO VISCOELASTIC-PLASTIC SOFT MATTER 28
      2.2.1 VISCOELASTIC-PLASTIC MODEL 29
      2.2.2 COMPUTATIONAL MODELLING WITH FINITE ELEMENT ANALYSIS 30
   2.3. EXAMINING THE APPLICABILITY OF THE FUNDAMENTAL RELATIONS IN THE OP METHOD TO THE VISCOELASTIC-PLASTIC MATERIALS 32
      2.3.1 EXAMINATION OF THE CORRELATION BETWEEN THE INSTANTANEOUS MODULUS, CONTACT STIFFNESS AND CONTACT AREA 34
      2.3.2 EFFECTS OF THE TIME-DEPENDENT DEFORMATION BEHAVIOR AND THE PLASTIC DEFORMATION ON THE DETERMINATION OF THE CONTACT AREA 38
   2.4 SIMULATION OF THE INDENTATION CREEP TESTS BY USING THE VISCOELASTIC-PLASTIC MODEL 42
   2.5 CONCLUSIONS 45
   REFERENCES 46

3. EXPERIMENTAL RESULTS 49
   3.1. NANOINDENTATION OF POLYMERS 49
   3.2. PRELIMINARY CHARACTERIZATION 51
      3.2.1 SURFACE ROUGHNESS 52
      3.2.2 TIP DEFECTS AND CALIBRATION 53
      3.2.3 INITIAL CONTACT POINT 56
      3.2.4 THERMAL DRIFT 56
<table>
<thead>
<tr>
<th>3.2.5.</th>
<th>MACHINE COMPLIANCE</th>
<th>57</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.3.</td>
<td>INDENTATION PROCEDURE</td>
<td>57</td>
</tr>
<tr>
<td>3.4.</td>
<td>MATERIALS STUDIED</td>
<td>58</td>
</tr>
<tr>
<td>3.5.</td>
<td>GENERAL CHARACTERISTICS OF THE CHOSEN POLYMERS USING INDENTATION</td>
<td>59</td>
</tr>
<tr>
<td>3.5.1.</td>
<td>INTRINSIC DEFORMATION BEHAVIOUR</td>
<td>59</td>
</tr>
<tr>
<td>3.6.</td>
<td>VALIDATING THE RESULTS FROM COMPUTATIONAL STUDY WITH EXPERIMENTS</td>
<td>65</td>
</tr>
<tr>
<td>3.6.1.</td>
<td>DETERMINATION OF THE INSTANTANEOUS MODULUS BY USING A SPHERICAL INDENTER</td>
<td>65</td>
</tr>
<tr>
<td>3.6.2.</td>
<td>CORRECTING THE MAXIMUM LOAD</td>
<td>70</td>
</tr>
<tr>
<td>3.7.</td>
<td>CONCLUSIONS</td>
<td>72</td>
</tr>
<tr>
<td>REFERENCES</td>
<td>73</td>
<td></td>
</tr>
<tr>
<td>4.</td>
<td>INFLUENCE OF SURFACE ENERGY</td>
<td>78</td>
</tr>
<tr>
<td>4.1.</td>
<td>SURFACE FORCES</td>
<td>78</td>
</tr>
<tr>
<td>4.2.</td>
<td>THEORITICAL MODELS</td>
<td>79</td>
</tr>
<tr>
<td>4.3.</td>
<td>IMPLEMENTING THE THEORIES FOR SOFT MATTER INDENTATION PROBLEM</td>
<td>84</td>
</tr>
<tr>
<td>4.3.1.</td>
<td>THEORETICAL ANALYSIS</td>
<td>85</td>
</tr>
<tr>
<td>4.4.</td>
<td>EXPERIMENTAL VERIFICATION OF THE THEORETICAL ANALYSIS USING NANOINDENTATION</td>
<td>89</td>
</tr>
<tr>
<td>4.5</td>
<td>CONCLUSIONS</td>
<td>94</td>
</tr>
<tr>
<td>REFERENCES</td>
<td>94</td>
<td></td>
</tr>
<tr>
<td>5.</td>
<td>IDENTIFYING THE LIMITATION OF OLIVER AND PHARR METHOD WITH RESPECT TO INDENTER GEOMETRY</td>
<td>97</td>
</tr>
<tr>
<td>5.1.</td>
<td>INTRODUCTION</td>
<td>97</td>
</tr>
<tr>
<td>5.2.</td>
<td>EXPERIMENTS</td>
<td>99</td>
</tr>
<tr>
<td>5.2.1.</td>
<td>MATERIALS</td>
<td>99</td>
</tr>
<tr>
<td>5.2.2.</td>
<td>NANOINDENTATION</td>
<td>99</td>
</tr>
<tr>
<td>5.2.3.</td>
<td>OLIVER &amp; PHARR METHOD</td>
<td>101</td>
</tr>
<tr>
<td>5.3.</td>
<td>RESULTS AND DISCUSSIONS</td>
<td>102</td>
</tr>
<tr>
<td>5.3.1.</td>
<td>COMPARING AREA FUNCTION FROM SPHERICAL AND BERKOVICH INDENTER</td>
<td>102</td>
</tr>
<tr>
<td>5.4.</td>
<td>CONCLUSIONS</td>
<td>109</td>
</tr>
<tr>
<td>REFERENCES</td>
<td>110</td>
<td></td>
</tr>
<tr>
<td>6.</td>
<td>CONCLUSIONS AND OUTLOOK</td>
<td>113</td>
</tr>
<tr>
<td>7.</td>
<td>APPENDIX</td>
<td>116</td>
</tr>
<tr>
<td>SCIENTIFIC CONTRIBUTIONS</td>
<td>121</td>
<td></td>
</tr>
<tr>
<td>CURRICULUM VITAE</td>
<td>122</td>
<td></td>
</tr>
</tbody>
</table>
### LIST OF SYMBOLS AND ABBREVIATIONS

#### Symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>(P)</td>
<td>Indenter load</td>
<td>N</td>
</tr>
<tr>
<td>(R)</td>
<td>Indenter radius</td>
<td>m</td>
</tr>
<tr>
<td>(E_r)</td>
<td>Reduced modulus</td>
<td>Pa</td>
</tr>
<tr>
<td>(E'_r)</td>
<td>Modulus of the indenter</td>
<td>Pa</td>
</tr>
<tr>
<td>(E)</td>
<td>Modulus of the specimen</td>
<td>Pa</td>
</tr>
<tr>
<td>(h_t)</td>
<td>Total depth of penetration</td>
<td>m</td>
</tr>
<tr>
<td>(\delta)</td>
<td>Indentation depth</td>
<td>m</td>
</tr>
<tr>
<td>(\lambda) and exponent (\beta)</td>
<td>Constants</td>
<td>-</td>
</tr>
<tr>
<td>(H)</td>
<td>Hardness</td>
<td>Pa</td>
</tr>
<tr>
<td>(P_{\text{max}})</td>
<td>Maximum load applied</td>
<td>N</td>
</tr>
<tr>
<td>(A_{\text{max}})</td>
<td>Contact area at maximum load</td>
<td>m²</td>
</tr>
<tr>
<td>(h_{\text{max}})</td>
<td>Maximum penetration</td>
<td>m</td>
</tr>
<tr>
<td>(S)</td>
<td>Unloading contact stiffness</td>
<td>N/m</td>
</tr>
<tr>
<td>(A)</td>
<td>Contact area</td>
<td>m²</td>
</tr>
<tr>
<td>(\gamma)</td>
<td>Constant - indenter geometry</td>
<td>-</td>
</tr>
<tr>
<td>(h_f)</td>
<td>Depth of the residual impression</td>
<td>m</td>
</tr>
<tr>
<td>(A(h_c))</td>
<td>Area function</td>
<td>-</td>
</tr>
<tr>
<td>(\kappa)</td>
<td>Geometric constant</td>
<td>-</td>
</tr>
<tr>
<td>(\sigma)</td>
<td>Total stress contribution from viscoelastic-plastic material</td>
<td>Pa</td>
</tr>
<tr>
<td>(\sigma_v)</td>
<td>Viscoelastic stress</td>
<td>Pa</td>
</tr>
<tr>
<td>(\sigma_p)</td>
<td>Viscoplastic stress</td>
<td>Pa</td>
</tr>
<tr>
<td>(\tau)</td>
<td>Relaxation time</td>
<td>s</td>
</tr>
<tr>
<td>(\eta)</td>
<td>Coefficient of viscosity</td>
<td>Pa.s</td>
</tr>
<tr>
<td>(E'_r)</td>
<td>Elastic moduli of the elastic-viscous network</td>
<td>Pa</td>
</tr>
<tr>
<td>(E'_p)</td>
<td>Elastic moduli of the elastoplastic network</td>
<td>Pa</td>
</tr>
<tr>
<td>(\sigma_y)</td>
<td>Initial yield stress</td>
<td>Pa</td>
</tr>
<tr>
<td>(g)</td>
<td>Work-hardening of the material</td>
<td>-</td>
</tr>
<tr>
<td>(\epsilon)</td>
<td>Total strain contribution from viscoelastic-plastic material</td>
<td>-</td>
</tr>
<tr>
<td>(R_w)</td>
<td>Radius of the substrate</td>
<td>m</td>
</tr>
<tr>
<td>(L_h)</td>
<td>Height of the substrate</td>
<td>m</td>
</tr>
<tr>
<td>(T)</td>
<td>Represents the traction force</td>
<td>-</td>
</tr>
<tr>
<td>(U)</td>
<td>Represents the displacement</td>
<td>-</td>
</tr>
<tr>
<td>(t_h)</td>
<td>Represent the holding time in the experimental protocol</td>
<td>s</td>
</tr>
<tr>
<td>(t_l)</td>
<td>Represent the loading time in the experimental protocol</td>
<td>s</td>
</tr>
<tr>
<td>(t_u)</td>
<td>Represent the unloading time in the experimental protocol</td>
<td>s</td>
</tr>
<tr>
<td>(v)</td>
<td>Poisson’s ratio</td>
<td>-</td>
</tr>
<tr>
<td>(v_h)</td>
<td>Initial unloading slope</td>
<td>N/m</td>
</tr>
<tr>
<td>(h_c)</td>
<td>Contact depth</td>
<td>m</td>
</tr>
<tr>
<td>(E_0)</td>
<td>Instantaneous modulus</td>
<td>Pa</td>
</tr>
<tr>
<td>(E'_w)</td>
<td>Long-term modulus</td>
<td>Pa</td>
</tr>
</tbody>
</table>
## LIST OF SYMBOLS AND ABBREVIATIONS

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_{c,1}$ and $R_{c,2}$</td>
<td>Ramp correction factors</td>
<td>-</td>
</tr>
<tr>
<td>$\sigma_s$</td>
<td>Maximum asperities height</td>
<td>m</td>
</tr>
<tr>
<td>$a_0^2$</td>
<td>Contact radius</td>
<td>m$^2$</td>
</tr>
<tr>
<td>$h^*$</td>
<td>Critical depth at which conical probe changes to sphere</td>
<td>m</td>
</tr>
<tr>
<td>$\theta$</td>
<td>Cone angle</td>
<td>$^0$</td>
</tr>
<tr>
<td>$\varepsilon_{\text{rep}}$</td>
<td>Characteristic strain</td>
<td>-</td>
</tr>
<tr>
<td>$\chi$</td>
<td>Surface energy</td>
<td>N/m</td>
</tr>
<tr>
<td>$\mu$</td>
<td>Tabors parameter</td>
<td>-</td>
</tr>
<tr>
<td>$Z_0$</td>
<td>Equilibrium separation between atoms</td>
<td>m</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>Maugis transition parameter</td>
<td>-</td>
</tr>
<tr>
<td>$K$</td>
<td>Combined elastic modulus of tip and sample</td>
<td>Pa</td>
</tr>
<tr>
<td>$m$</td>
<td>Ratio of the outer radius to the contact radius</td>
<td>-</td>
</tr>
<tr>
<td>$a_n$</td>
<td>Normalized contact radius</td>
<td>m</td>
</tr>
<tr>
<td>$P_n$</td>
<td>Normalized indentation load</td>
<td>N</td>
</tr>
<tr>
<td>$\delta_n$</td>
<td>Normalized indentation depth</td>
<td>m</td>
</tr>
<tr>
<td>$\delta_0$</td>
<td>Maugis contact depth</td>
<td>m</td>
</tr>
<tr>
<td>$P_{r,H}$</td>
<td>Indentation load calculated using hertzian solution</td>
<td>N</td>
</tr>
<tr>
<td>$P_r$</td>
<td>Indentation load calculated using maugis theory</td>
<td>N</td>
</tr>
<tr>
<td>$h_{\text{cri}}$</td>
<td>Critical indentation depths</td>
<td>m</td>
</tr>
<tr>
<td>$L_c$</td>
<td>Normalized value of the pull-off force</td>
<td>N</td>
</tr>
<tr>
<td>$\chi_I$</td>
<td>Surface energy of the indenter</td>
<td>N/m</td>
</tr>
<tr>
<td>$\chi_S$</td>
<td>Surface energy of the polymer</td>
<td>N/m</td>
</tr>
<tr>
<td>$\chi_{I-S}$</td>
<td>Interface energy between the indenter and the polymer</td>
<td>N/m</td>
</tr>
<tr>
<td>$L_c$</td>
<td>Pull-off force</td>
<td>N</td>
</tr>
</tbody>
</table>

## ABBREVIATIONS

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>DSI</td>
<td>Depth sensing indentation</td>
</tr>
<tr>
<td>OP</td>
<td>Oliver and Pharr method</td>
</tr>
<tr>
<td>DC</td>
<td>Displacement controlled mode</td>
</tr>
<tr>
<td>LC</td>
<td>Load controlled mode</td>
</tr>
<tr>
<td>AFM</td>
<td>Atomic force microscope</td>
</tr>
<tr>
<td>FE-SEM</td>
<td>Field Emission Scanning Electron Microscope</td>
</tr>
<tr>
<td>PMMA</td>
<td>Polymethyl metha acrylate</td>
</tr>
<tr>
<td>PP</td>
<td>Polypropylene</td>
</tr>
<tr>
<td>LDPE</td>
<td>Low-density polyethylene</td>
</tr>
<tr>
<td>PET</td>
<td>Polyethylene terephthalate</td>
</tr>
<tr>
<td>PS</td>
<td>Polystyrene</td>
</tr>
<tr>
<td>PDMS</td>
<td>Polydimethylsiloxane</td>
</tr>
<tr>
<td>DMT</td>
<td>Derjaguin–Muller–Toporov</td>
</tr>
<tr>
<td>JKR</td>
<td>Johnson–Kendall–Roberts</td>
</tr>
<tr>
<td>MD</td>
<td>Maugis–Dugdale</td>
</tr>
</tbody>
</table>
CHAPTER 1

1. INTRODUCTION

1.1 MOTIVATION

The conventional techniques for mechanical testing are uniaxial tests in tension or compression, bend tests or cyclic testing, which all have the following features in common. Specimens of macroscopic dimensions (sizes of several mm and g-quantities) are needed, the load resolution is in mN-range and they are time consuming due to little test automation. Contrary to this the ongoing trend in industrial and research development is towards miniaturization and automation, which requires adequate methods to mechanically characterize structures in the sub-μm range. In many cases the mechanical behavior is the determining factor for the performance and life time, not only in the construction of load bearing or structural components, but also for the application of materials as functional components and for the biological function of body parts. It also offers a favorable means for the investigation of the mechanical behavior of thin films and coatings, which is essential for many technical applications, e.g. for microelectronic devices and protective coatings. The determination of mechanical properties of materials such as elastic modulus and hardness by means of nanoindentation has become more and more popular in recent years. This technique, also termed as depth-sensing indentation (DSI), used to study the mechanical behavior for a wide range of materials like, metallic, polymeric, biological, ceramic or engineering materials.

DSI have been used for very intricate studies where all the conventional tools fails to extract properties. The occurrence of force discontinuities in nanoindented semicrystalline polymer is related to local variations and anisotropy in the properties of the crystalline lamellar aggregates. The mechanical heterogeneity emerging from contact interactions between an extremely sharp tip and the nanoscale morphology of semicrystalline polymers is studied using the plastic pile-ups left around the indents. Ioannis Karapanagiotis developed a criterion to...
predict the resulting evolution process of surface defects on thin polystyrene films on silicon substrate using nanoindentation-induced indents under various experimental conditions. Poilane et al.\textsuperscript{11}, studied the mechanical properties of a thin film of polyurethane shape memory polymer using nanoindentation. A weak residual stress and viscoelastic behavior of the material has been determined using DSI. Kermouche et al.\textsuperscript{12} proposed a solution which allows to relate the classic nanoindentation results – mean pressure or hardness, elastic modulus, indentation strain rate – to the representative parameters: the representative stress, strain and strain rate of the indentation test. The practical interest of this method is that it gives very easily and quickly a first approximation of the stress–strain curves of elastic–viscoplastic materials using two indenters. The application of nanoindentation to soft matter has increased over recent years. The lateral spatial resolution of nanoindentation allows local testing of mechanical properties in tissues that is not possible using macroscale techniques. In the biological field more and more knowledge is gained about processes, which are strongly dependent on the mechanical properties of the related tissues or materials. The application of nanoindentation testing to biological tissues often is motivated by medical interests, since many diseases are associated with altered or altering mechanical properties of the respective biological tissues\textsuperscript{13}. In different studies\textsuperscript{14,15} it was possible to correlate areas of reduced mineral content in the human dental enamel with decreased modulus and hardness values. These regions of lower mineral content and reduced properties were exactly the positions, where lesion and cavity formation occurred later on. Leong and Morgan\textsuperscript{16} used nanoindentation to describe local changes in the mineralization across a rat fracture callus. Ferguson et al.\textsuperscript{17} applied the same technique to human articular calcified cartilage and subchondral bone from normal and osteoarthritic patients.

Yet, the nanoindentation instruments still are designed for the use on hard and stiff materials, so their usage on soft samples makes it very difficult to obtain accurate results and poses questions that are still to answer. There are several unique challenges associated with applying nanoindentation to soft materials. Major sources of difficulty include evaluating the appropriateness of mechanical models (Cheng et al.,)\textsuperscript{18}, defining suitable calibration materials
(Bushby; Klapperich et al.; Odegard et al.;), characterizing and maintaining sample hydration (Bembey et al.,), and eliminating other sources of experimental error in the measurements (Cao et al.,). Again, this underlines the need for the development of techniques, or improving the available techniques for time dependent materials (soft matter). Oyen examined nanoindentation creep experiments in polymers following ramp loading. Cheng et al., derived a solution for standard linear solid materials indented with a spherical tip geometry. Fujisawa et al., studied the viscoelasticity of polymethylmethacrylate (PMMA) by quantifying the strain dependence of the elastic modulus from nanoindentation. Nanoindentation is one of the most promising techniques for the application in mechanical testing of soft materials and also small volumes, because the instrumentations possess many of the features, which are needed in this respect. Testing equipment and methods underwent a continuous improvement. In recent years researchers have combined various tools for obtaining combinatorial information from DSI. Contact stiffness measurement (Syed Asif et al.,) combines traditional Atomic Force Microscope with a depth sensing system. Contact stiffness measurement refers to the mapping of elasticity by using force modulation techniques. Such a force modulation setup has the great advantage that it supplies quantitative images of mechanical properties that are easily to interpret. Foschia et al., combined two distinctive measurement techniques, local mechanical spectroscopy and mechanical imaging modes which allows them to perform Local-Dynamic Mechanical Analysis (L-DMA). This setup allows them for quantitative imaging of storage and loss modulus of a material. It is possible to characterize highly heterogeneous samples consisting of several chemical phases on a submicrometer level. Tweedie combined instrumented indentation and SPM (Scanning Probe Microscopy) imaging to demonstrate the post-indentation viscoelastic recovery with simple linear models.

1.2 NANOINDENTATION BACKGROUND

The indentation hardness test, where an indenter induces a localized deformation into a solid surface, is a relatively simple and virtually non-destructive means of assessing mechanical
properties of several solids. The most commonly used hardness measurements are: scratch hardness and static hardness. Scratch hardness is the oldest form of hardness measurement. It depends on the ability of one material to scratch another or to be scratched by another solid. The method most widely used in determining the hardness of materials are static indentation methods. In a conventional indentation hardness test, the contact area is determined by measuring the indentation size using a microscope after the sample is unloaded. More recently, in DSI hardness tests, the contact area has been determined by measuring the indentation depth during loading-unloading cycle. Indentation load-displacement data contains a wealth of information. Among the mechanical properties of interest, one or more of which can be obtained using commercial and specialised indentation testers, are elastic-plastic deformations behaviour, hardness, Young’s modulus, scratch resistance, film-substrate adhesion, residual stresses, time dependent creep and relaxation properties, fracture toughness and fatigue.

1.2.1 REVIEW OF MATHEMATICAL MODELS

Regardless of the type of instrument used in nanoindentation tests, extraction of elastic properties from the raw data entails the fitting of mathematical models of deformation behavior to the load-displacement (in the case of the nanoindentation) or deflection-position data (in the case of the AFM). The models used are predominantly based on classic linear elasticity theory, with the fundamental conditions of material isotropy and homogeneity, infinitesimal indentation (i.e., small indentation depth and probe size in relation to sample size), and deformations that do not exceed the linear stress-strain regime. The seminal work in the field of contact mechanics is attributed by Hertz, who solved the problem of elastic contact between two ellipsoidal bodies. The special case of indentation allows simplification of the contact problem to that of one between an elastic half-space and a rigid probe of well-defined geometry, first considered by Boussinesq shortly following publication of Hertz’s work. Numerous others (e.g., Love, and Sneddon) have contributed to the theoretical framework to the point where exact solutions in the form of force-indentation relationships, contact
pressure distributions, and stress and displacement fields are available for common axisymmetric geometries (e.g., cylinder, sphere, and cone). When the indenter is spherical in shape, the resulting force-indentation relationship is often referred to as the Hertz equation. It is also common to refer to linear elastic contact as being “Hertzian.” Hertz found that the radius of the circle of contact \( a \) is related to the indenter load \( P \), the indenter radius \( R \), and the elastic properties of the contacting material by equation (1.1):

\[
a^3 = \frac{3PR}{4Er}
\]  

(1.1)

The quantity \( Er \) (reduced modulus) combines the modulus of the indenter and the specimen and is given by equation (1.2):

\[
\frac{1}{Er} = \frac{(1\cdot v^2)}{E} + \frac{(1\cdot v'^2)}{E'}
\]  

(1.2)

where \( E \) and \( v \) are Young’s modulus and Poisson’s ratio of the sample, the primed terms apply to the indenter properties. Hertz equation are concerned with the localized deformation at the contact and not the bulk deformation, the load depth relation is given by equation (1.3),

\[
P = \frac{4}{3} Er \frac{1}{R^2} h_t^2
\]  

(1.3)

where \( h_t \) is the total depth of penetration beneath the specimen free surface. Solutions for different indenter geometries commonly used in indentation can be represented by the generalized force-indentation relation (1.4):

\[
P = \lambda \delta^\beta
\]  

(1.4)
where $P$ is the force applied to the indenter, $\delta$ is the indentation depth, and the terms $\lambda$ and exponent $\beta$ are constants. Value of the exponent $\beta$ for some common punch geometries are $\beta=1$ for flat cylinders and for paraboloids of revolution, $\beta=2$ for cones, and $\beta=1.5$ for spheres in the limit of small displacements.

1.3 ANALYSIS OF NANOINDENTATION DATA

Nanoindentation is conventionally performed using the instrumented indentation whereby the load and the indenter displacement are recorded during the indentation process. Both loading and unloading responses are recorded in the form of a load-displacement curve. During a quasi-static test a continuously increasing force is applied to the indenter tip until a certain load level (i.e. load-control) or penetration depth (i.e. displacement control) is reached, and then the indenter is unloaded again. The resulting load-displacement response typically shows an elastic-plastic loading followed by an elastic unloading, fig.1.1. During the loading segment a hardness impression is formed as a result of elastic and/or plastic deformation occurring under the indenter tip. Upon the withdrawal of the tip the elastic portion of the deformation recovers and thus allows the elastic modulus of the material to be quantified. The amount of plastic deformation in the specimen can be identified from the permanent hardness impression. Here, the hardness, $H$ is defined as the mean pressure under the indenter tip and is calculated according to equation (1.5):

$$H = \frac{P_{\text{max}}}{A_{\text{max}}}$$

(1.5)

where $P_{\text{max}}$ is the maximum load applied and $A_{\text{max}}$ is the contact area at maximum load. In this section, methods of the analysis of nanoindentation data are presented in detail.
In early 1980 it was realised that load depth sensing indentation methods could be very useful for measuring small volumes. Oliver, Hutchings, and Pethica suggested a simple method based on measured load-displacement curves and a knowledge of the indenter area function, that is the cross-section area of the indenter as a function of distance from its tip. Doerner and Nix proposed a simple empirical method and suggested that the unloading stiffness can be computed from a linear fit of the upper one-third of the unloading curve. Oliver and Pharr used, the elastic equation of contact in conjunction with the unloading data to determine the elastic modulus and hardness of the material. For the calculation of the elastic modulus from the unloading curve two equations are needed equations (1.6) and (1.9).

\[ E_r = \frac{S\sqrt{\pi}}{2\gamma\sqrt{A}} \]  

(1.6)

In equation (1.6), \( S \) is the unloading contact stiffness, \( A \) the contact area, \( \gamma \) is a constant.
depending on the indenter geometry and $E_r$ is the reduced modulus. In order to gain the elastic modulus from equation (1.6) the determination of the unloading contact stiffness and the contact area are necessary first. Therefore the unloading curve is fitted to a power-law relation proposed by Oliver and Pharr $^1$.

\[
P = B \cdot (h - h_f)^m
\] (1.7)

\[
S = \frac{dp}{dh} = Bm(h - h_f)^{m-1}
\] (1.8)

Here $P$ is the applied load, $h$ is the resulting penetration, $h_f$ is the depth of the residual impression and $B$, $m$ are fitting parameters. The analytical differentiation of equation (1.8) delivers the slope of the unloading curve $dP/dh$, which is equivalent to the unloading stiffness $S$ when evaluated at the maximum penetration $h_{\text{max}}$. As can be seen from equations (1.5) and (1.6) the determination of the contact area is important for achieving exact results from indentation testing. The area function $A(h_c)$, which is used to compute the contact area $A$, geometrically relates the projected, i.e. the cross-sectional area of the indenter tip to the distance from its apex. The overall displacement of the indenter is the sum of the contact depth and the surface displacement, which can be seen from the schematic sketch in fig.1.2, where all the quantities used in the analysis are illustrated.

\[
A = f(h_c) \quad \text{and} \quad h_c = h_m - \kappa \frac{F_m}{S}
\] (1.9)

Here $\kappa$ being a geometric constant with a value of 0.72 for a conical indenter tip, 0.75 for a paraboloid of revolution and 1 for a flat punch. Once the contact depth has been determined for an indentation, the contact area is simply the value of the area function at the contact
depth \( A (h_c) \). The area function \( A (h_c) \) itself is calibrated for each tip individually by indenting a fused silica or quartz standard of known modulus and calculating the contact area.

The OP method uses the slope of the tangent to the unloading data at maximum load in conjunction with the derivative of the elastic equations of contact for an equivalent conical indenter to determine the depth of the circle of contact. The contact area is obtained from the unloading curve for determining the hardness and Young’s modulus. The OP method is the most widely used method, due to the commercialization of instruments with only this analysis built in. An alternative method uses the unloading data directly with elastic equation of contact and this method was first proposed by Field and Swain \(^{36}\).

1.4 SCOPE OF THIS THESIS

Extensive usage of nanoindentation in conjunction with the OP method and the series uncertainties reported recently for viscoelastic-plastic materials have brought alerts to the growing soft matter nanoindentation community. In particular, the estimated elastic modulus is several times larger than the correct one, thus challenging the possibility of a nanomechanical characterization of polymers. Viscoelasticity, pile-up, or adhesive forces is usually blamed for
this failure. Considering the limitations in the OP method, a number of novel methods\textsuperscript{37-41} have been proposed in recent years to determine the compliance functions or the relaxation functions of the viscoelastic-plastic materials (soft matter). These methods are mainly based on the solutions of the elastic contact problems and the correspondence principle\textsuperscript{27-29}. The objective of the present thesis is to address the following important issues with respect to OP method. In this study, a number of fundamental issues regarding the use of nanoindentation tests to determine the mechanical properties of viscoelastic-plastic soft matter are addressed.

1) Ngan et al.\textsuperscript{38,39} and Cheng et al.\textsuperscript{40} have proposed novel procedures to determine the initial unloading slope which can be reliably applied to both linearly viscoelastic materials and nonlinear viscoelastic materials. Taking into consideration that in the indentation of some polymeric materials and biological materials, the indented solids may undergo both \textit{viscoelastic} and \textit{plastic} deformation; it is interesting and useful to study the applicability of the procedures proposed by Ngan et al.\textsuperscript{38,39} and Cheng et al.\textsuperscript{40} to these circumstances. The plastic deformation and the time-dependent deformation behavior on the fundamental relations in the Oliver & Pharr method are studied by using finite element analysis based on a viscoelastic-plastic model developed for polymers.

2) The methods\textsuperscript{42-44} based on the indentation creep tests and the constant loading rate tests have been presented recently to determine the viscoelastic properties of the soft matter, e.g. the compliance function or the relaxation function of the polymers. It is noted that for the spherical indentation of the common polymers (e.g. polycarbonate, polystyrene), the indented may undergo plastic deformation; depending on the ratio of the indentation depth to indenter radius. Therefore, it is necessary and useful to identify the extent to which the plastic deformation will affect the performance of the novel methods.

3) For the indentation of soft matter, the effects of adhesion may come into play. There are a number of famous models\textsuperscript{45-47} in the literature for the adhesive contact of a spherical indenter with an elastic half-space. There are also quite a few publications\textsuperscript{48} which use these classic models to analyze the adhesive indentation response. For the methods concerned in this
study (e.g. the OP method\textsuperscript{1} and the methods based on the indentation creep tests \textsuperscript{42, 44}, the effects of adhesion are not taken into consideration. Therefore, in the use of these methods, one may simply need to know the critical indentation depths beyond which the influence of adhesion can be omitted. In this case, it is useful to propose the results valid for the general adhesive contact problems, from which the common users can easily estimate such critical indentation depths without invoking the adhesive contact theories.

Based on the issues above, research as outlined below has been performed.

i) Computational modeling of the spherical indentation is carried out by using a viscoelastic-plastic model developed for polymers. The intention is to examine the applicability of the two fundamental relations in the OP method when the indented materials undergo viscoelastic and plastic deformation. The analysis eventually leads to a loading-holding-unloading protocol for a displacement-controlled machine; based on which and using the OP method, the instantaneous modulus of the viscoelastic-plastic materials may be reliably determined. Furthermore, the effects of the plastic deformation on the methods based on the indentation creep tests to determine the viscoelastic properties is also studied.

ii) Using the MD\textsuperscript{47} (Maugis-Dugdale) model, a general relation characterizing the effects of adhesion will be presented (which applies to the JKR and DMT model as well). The result permits to easily determine the critical indentation depths beyond which the effects of adhesion is negligible without invoking the original theories.

iii) Experiments are performed on four kinds of polymers, to validate some conclusions drawn from the numerical and theoretical analysis. The experiments are initially performed using a spherical indenter. Further we made an attempt to extend the results from spherical indenters to berkovich geometry.

This systematic study can help us understand the actual limitation of the OP method for viscoelastic-plastic materials.
REFERENCES:


10. Ioannis Karapanagiotis: An energetic criterion to compare the evolution of thermally excited surface disturbances and nanoindentation-induced defects on thin polymer films, Surface Science, 601, 2007, 3426


31. B. Bhushan, and Xiaodong Li: Nanomechanical characterization of solid surfaces and thin films, International Materials Reviews, 48, 2003, 125


33. A. E. H. LOVE: Boussinesq's Problem for a Rigid Cone, Oxford, 1939, 161


46. B. V. Derjaguin, V. M.Muller, Y. P. Toporov: Effect of contact deformations on the adhesion of particles, J. Colloid Interface Sci., 53, 1975, 314


CHAPTER 2

2. COMPUTATIONAL STUDIES

2.1 INTRODUCTION

Nanoindentation tests are widely used in recent years to characterize the mechanical properties of time-dependent materials at the micro or nano-scale\textsuperscript{1-2}. In most cases, the procedure proposed by Oliver and Pharr\textsuperscript{3} (OP method) by improving the method of Doerner and Nix is adopted. However, recent studies\textsuperscript{4-9} revealed that the mechanical properties of time-dependent materials determined using the OP method might exhibit significant errors. Hochstetter et al.,\textsuperscript{4} showed that the OP method suffers from the effect of the time-dependent deformation behavior of polymers. They recommended using a holding segment and a fast unloading procedure to overcome the effect of creep. At the same time, they presented a new scheme to evaluate the projected contact area. Recently, Ngan et al.,\textsuperscript{5,6} and Cheng et al.,\textsuperscript{7} have proposed novel procedures to determine the initial unloading slope for the indentation of viscoelastic materials. Cheng et al.,\textsuperscript{8} showed that for the indentation of viscoelastic materials, the indentation loads at given indentation depth depend on the loading rates; but the initial unloading slopes corresponding to different loading rates are the same. This indicates that the contact depth determined using the procedure suggested by Oliver and Pharr depends on the loading rates. Thus the Young’s modulus given by the OP method in this case may not be reliable. More recently Tranchida et al.,\textsuperscript{9} have performed comprehensive analysis on the applicability of the OP method and concluded that it was incorrect to use the OP method to the characterization of the polymers exhibiting viscoelastic-plastic deformation since the method is based on elastic analysis. Furthermore, they suggested that viscoelastic mechanics models should be applied to analyze the nanoindentation data\textsuperscript{10}. The contributions above help understand the limitations of the OP method in the mechanical characterization of time-dependent materials. But taking the following fundamental issues into consideration, further
investigation on the applicability of the OP method is still necessary and important. Thus, the objective of the present study is to address the following important issues.

1) Ngan et al., 5,6 and Cheng et al., 7 have proposed novel procedures to determine the initial unloading slope which can be reliably applied to both linearly viscoelastic materials and nonlinear viscoelastic materials. Taking into consideration that in the indentation of some polymeric materials and biological materials, the indented solids may undergo both viscoelastic and plastic deformation; it is interesting and useful to study the applicability of the procedures proposed by Ngan et al., 5,6 and Cheng et al., 7 to these circumstances. In addition, in the presence of viscoelastic deformation, Cheng et al., 7 show that the OP method with or without the correction of Ngan et al., 6 cannot be used to correctly evaluate the contact area. Thus they propose to use the correlation between the contact depth and indentation depth to determine the contact area. But their method 8 is only for viscoelastic materials and ideal indenter geometries. In the case that the plastic deformation occurs or the indenter has tip defects, the method 7 may be invalid. Due to the plastic deformation, the indented material might exhibit piling-up; in this case, the OP method will underestimate the contact area and thus overestimate the reduced modulus. Bearing this point in mind, it is still necessary and useful to investigate to what extent the contact area can be well determined by using the OP method, when the indented material simultaneously undergoes the viscoelastic and plastic deformation.

2) Considering the limitations in the OP method, a number of novel methods 4-13 has been proposed in recent years to determine the compliance functions or the relaxation functions of the soft matter. These methods are mainly based on the solutions of the elastic contact problems and the correspondence principle. The methods 14-17 based on the indentation creep tests and the constant loading rate tests have been presented recently to determine the viscoelastic properties of the soft matter, e.g. the compliance function or the relaxation function of the polymers. It is noted that for the spherical indentation of the common polymers (e.g. polymethyl metha acrylate (PMMA), polycarbonate (PC), polystyrene (PS) and so on), indented
polymers may undergo plastic deformation; depending on the ratio of the indentation depth to indenter radius. However, the methods \cite{14-17} to determine the viscoelastic properties based on indentation creep tests and the constant loading rate tests are derived by using the elastic contact solutions and the correspondence principle \cite{15-17}. Therefore, it is necessary and useful to identify the extent to which the plastic deformation will affect the performance of the novel methods.

Based on the issues above, research as outlined below has been performed.

i) Computational modeling of the spherical indentation is carried out by using a viscoelastic-plastic model developed for polymers. The intention is to examine the applicability of the two fundamental relations in the OP method when the indented materials undergo viscoelastic and plastic deformation. The analysis eventually leads to a loading-holding-unloading protocol for a displacement-controlled machine; based on which and using the OP method, the instantaneous modulus of the viscoelastic-plastic materials may be reliably determined.

ii) Using the viscoelastic-plastic model, finite element analysis is performed to study the effects of the plastic deformation on the methods based on the indentation creep tests to determine the viscoelastic properties. The objective is to identify the upper limits of the ratios of the indentation depth to the indenter radius, beyond which the effects of plastic deformation are significant.

2.2 COMPUTATIONAL MODELLING OF THE SPHERICAL INDENTATION INTO VISCOELASTIC-PLASTIC SOFT MATTER

In this section, computational modeling of the spherical indentation into viscoelastic-plastic soft matter is carried out. The objective is to examine the applicability of the two fundamental relations in the OP method on the one hand; and on the other hand to study effects of plastic deformation on the indentation creep tests \cite{15,17} in determining the viscoelastic properties of the materials.
2.2.1 VISCOELASTIC-PLASTIC MODEL

Kichenin et al,\textsuperscript{18} found that two dissipative mechanical models are capable of predicting the nonlinear behaviour of polymers. A simple Maxwell model and an elastoplastic model with kinematic hardening are used to study the real polymers mechanical response. Maxwell model consists of a spring and dashpot in series describes the stress relaxation of a viscoelastic solid to a first approximation. Elastoplastic model is characterized by a threshold, and is necessary to account for the existence of residual stress, where stresses should completely decay after some time. This model has five coefficients: elastic moduli of the elastic-viscous network $E_v$, and viscosity coefficient $\eta$ for the Maxwell mechanism; elastic moduli of the elastoplastic network $E_p$, the initial yield stress $\sigma_y$, and the work-hardening of the material $g$ for elastoplastic model, fig.2.1.

![Viscoelastic Plastic Model](image)

Fig. 2.1 The viscoelastic plastic model used in the present analysis

The constitutive equations are described taking into account the stress relaxation, geometrical recovery and strain rate effects to study the real structures. Assuming the mechanisms are independent, the relaxation step and the geometrical recovery step isolate the elastoplastic mechanism part of the behaviour after relaxation, this very mechanism withstands the overall stress and after geometrical recovery, the eventual
Residual strain is connected to some movements of the slide. The constitutive equation for the model reads,

$$\sigma = \sigma_v + \sigma_p$$

$$\sigma_v = \eta \varepsilon_v = E_v (\varepsilon - \varepsilon^*)$$

$$\sigma_p = E_p \varepsilon = E_p (\varepsilon_c + g(\varepsilon - \varepsilon_c))$$

$$\varepsilon_c = \frac{\sigma_y}{E_p}$$

The choice of Maxwell model without thermal activation leads us to evaluate a relaxation time $\tau$, equation (2.4) and the elastoplastic model is well adopted to give an account of the memory effect of the material.

$$\tau = \eta / E_v$$

The finite element code built upon this model was used in simulating the cyclic pressure test on a polymer pipe specimen, and is applicable to our scientific concern.

**2.2.2 COMPUTATIONAL MODELLING**

Finite element analysis was performed by using a viscoelastic-plastic model which is explained above\textsuperscript{18, 19}. For a one-dimensional problem, the model is schematically shown in fig. 2.1. When $\sigma_y$ is taken as infinity, the model degenerates to the well known three-element linearly viscoelastic model. For the sake of simplicity, only perfectly plastic cases (i.e., $g = 0$) are investigated in the present study, in which piling-up of the indented material is more significant than that of the materials with the same ratio of the Young’s modulus to the yield strength but exhibiting plastic hardening. Detailed information of the model can be found elsewhere\textsuperscript{18, 19}. It is noted that Huber et al.,\textsuperscript{20-22} have proposed systematic inverse approaches to determine the material properties using indentation tests based on an elastic–viscoplastic model suited for metallic materials.

Although the model is simple, it has been shown that it can represent the viscoelastic-plastic deformation behavior of some typical polymers to the first order\textsuperscript{18}. The following property range is investigated in the present study: $\sigma_y / E_p$ varies from
0.1 to 0.01 and $E_v / E_p$ varies from 0.1 to 10. This range should include many common polymers. It is well known that the OP framework is based on the Sneddon’s solution, which deals with the contact of an axisymmetric indenter with an elastic half-space. However, in practice, the OP method is always applied to analyze the nanoindentation data from a Berkovich indenter; and in the analysis, the Berkovich indenter is assumed to be equivalent to a cone. Lim and Chaudhri argued that such equivalence may be invalid for the indentation of polymers. In addition, the deformation of the polymers strongly depends on the indenter geometry. The deformation of the indented materials may be very complicated for a Berkovich indenter and the material model as given by fig. 2.1 may fail to represent the real deformation behavior of the polymers in this case. Therefore, we focus on spherical indentation in our simulations. The axisymmetric model used in the computations is given by fig. 2.2. Based on the fact that the common diamond indenter is much harder than the typical polymers, the indenter is assumed to be rigid in the simulations. The indenter tip radius is taken as $R = 2 \mu m$. The radius $R_w$ and the height $L_h$ of the substrate are taken as $50 \mu m \times 50 \mu m$. The boundary conditions on the indented solid are specified such that the outer surface nodes are traction-free with fixed lower surface nodes as given by fig. 2.2 and the following equations:

$$T_r(r = R_w) = 0, \quad T_z(r = R_w) = 0 \quad \text{(outer surface)}; \quad (2.5)$$

and

$$U_r(z = L_h) = 0, \quad U_z(z = L_h) = 0 \quad \text{(lower surface)}; \quad (2.6)$$

where $T$ represents the traction force, and $U$ represents the displacement. Fig. 2.3 shows the finite element mesh. A total of 10,000 four-node bilinear axisymmetric reduced-integration elements with hourglass control are used to model the semi-infinite substrate of the indented solid. The convergence of the simulations has been examined by comparing the results with a refined mesh.
2.3 EXAMINING THE APPLICABILITY OF THE FUNDAMENTAL RELATIONS IN THE OP METHOD TO THE VISCOELASTIC-PLASTIC MATERIALS

The OP method is based on the following two fundamental relations,\(^3\)

\[ E_r = \frac{\sqrt{\pi} S}{2\gamma \sqrt{A}} \]  \hspace{2cm} (2.7)

\[ A = f(h_c) \quad \text{and} \quad h_c = h_m - \kappa \frac{F_m}{S} \]  \hspace{2cm} (2.8)

where \( E_r, S, A \) are the reduced modulus, the initial unloading slope and the projected contact area, respectively. The contact area \( A \) is related to the contact depth \( h_c \) by the area function \( f \). The correction factor \( \gamma \) in equation (2.7) used in most cases is due to King\(^25\) in order to correct the effects of the indenter geometry. In recent years there are some novel interpretations on this factor\(^26, 27\). \( h_m \), and \( F_m \) are the maximum
indentation depth and the load respectively. $\kappa$ is a constant, depending on the indenter shape; for a blunt tip, for instance the spherical indenter, $\kappa$ is 0.75. In the sequel, the fundamental relations given by equations (2.7) and (2.8) have been examined by using finite element analysis based on the material model given by fig. 2.1.
2.3.1. EXAMINATION OF THE CORRELATION BETWEEN THE INSTANTANEOUS MODULUS, CONTACT STIFFNESS AND THE PROJECTED CONTACT AREA

The fundamental relation given by equation (2.7) can be derived from the theory of elastic contacts. Based on Sneddon’s solution 23 Pharr et al. 28 have shown that equation (2.7) is valid for the contact of an axisymmetric rigid indenter with arbitrary profile with an elastic half-space. Recently, Cheng and Cheng 8, 29 further showed that this fundamental relation is also true for the indentation of linearly viscoelastic solids provided that the unloading rate is sufficiently fast. However, in the case that the indented materials simultaneously exhibit both, viscoelastic and plastic deformation, it is not clear if equation (2.7) is still applicable. In the present study, this issue is examined by using finite element computations based on the material model given by fig. 2.1. A trapezoidal displacement-controlled loading-holding-unloading procedure as given by fig.2.4 is used in the present work. \( t_h, t_l \) and \( t_u \) in the figure, represent the holding, loading and unloading time, respectively. \( t_l / \tau, t_h / \tau \) and \( t_u / \tau \) are varied in a wide range in the simulations. Three sets of material properties are used as examples; i.e., Mat1: \( E_v =200\text{MPa}, \quad E_p =1800\text{MPa}, \quad \sigma_y =18\text{MPa} \) and \( \nu =0.4 \); Mat2: \( E_v =1800\text{MPa}, \quad E_p =200\text{MPa}, \quad \sigma_y =2\text{MPa} \) and \( \nu =0.4 \); and Mat3: \( E_v =1800\text{MPa}, \quad E_p =200\text{MPa}, \quad \sigma_y =20\text{MPa} \) and \( \nu =0.4 \) refer, table 2.1.

Table 2.1 Materials used in the simulations to examine the two fundamental relations in the OP method (for all the cases, Poisson’s ratio is taken as 0.4)

<table>
<thead>
<tr>
<th>Materials</th>
<th>( E_v ) (MPa)</th>
<th>( E_p ) (MPa)</th>
<th>( \sigma_y ) (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mat 1</td>
<td>200</td>
<td>1800</td>
<td>18</td>
</tr>
<tr>
<td>Mat 2</td>
<td>1800</td>
<td>200</td>
<td>2</td>
</tr>
<tr>
<td>Mat 3</td>
<td>1800</td>
<td>200</td>
<td>20</td>
</tr>
</tbody>
</table>
The ratio of the maximum indentation depth to the indenter radius is taken as $h_m / R = 0.1$. The initial unloading slopes corresponding to different unloading rates and the holding time are given by fig. 2.5. The results in the figure are normalized by the convergent solutions which correspond a very fast unloading rate ($t_u = 0.01 \tau$); which
confirm the finding of Hochstetter et al., i.e., the holding time has a significant influence on the determination of the initial unloading slope. The results show that when the holding time is much longer than relaxation time (fig. 2.5(a)), even the unloading time is comparable with the relaxation time; the errors in the initial unloading slope are still small. When the holding time is shorter (fig. 2.5(b)), a faster unloading rate (e.g. \( t_u < 0.1\tau \)) is necessary to obtain a converged \( S \). Using the converged initial unloading slope and the projected contact area obtained directly from the deformed finite element mesh at maximum indentation depth, the instantaneous modulus is determined via equation (2.7). The results are 2100MPa (Mat1), 2080MPa (Mat2) and 2001MPa (Mat3), respectively; which match the exact solution (2000MPa) remarkably well. For the indentation of linearly viscoelastic materials, Cheng and Cheng \(^7\) show that equation (2.8) holds true provided the unloading rate is sufficient fast. The computational results in this study as given above show that equation (2.8) is even valid for the indentation of the viscoelastic-plastic materials as represented by the model in fig.2.1. Based on the rigorous theoretical analysis, Cheng et al., \(^8\) also show that for the indentation of linearly viscoelastic materials, the following relation holds true for a displacement-controlled machine,

\[
E_r = \frac{\sqrt{\pi} S_e}{2\sqrt{A}}
\]  

(2.9)

where \( S_e \) is given by

\[
S_e = \frac{dF}{dh}\bigg|_{h=h_u} + \frac{dF}{dt}\bigg|_{t_u} v_h
\]  

(2.10)

where \( \frac{dF}{dh}\bigg|_{h=h_u} \), \( \frac{dF}{dt}\bigg|_{t_u} \), \( v_h \) are the initial unloading slope, the relaxation rate of the load immediately before the unloading and the unloading rate, respectively. Equation (2.10) is also examined by using finite element analysis and the three sets of material properties given above. It is interesting to find from the computational results that although equation (2.10) is derived from the indentation of linearly viscoelastic
materials, it works very well also for the indentation of viscoelastic-plastic materials as represented by fig.2.1 (see fig. 2.5(b) for detail).

Fig.2.5 Effects of the holding time and the unloading rate on the initial unloading slope.
Equation (2.10) may be used to explain why the holding time plays an important role. $\frac{dF}{dt}\cancel{t}$ in equation (2.10) depends on the holding time; and for a long holding time, $\frac{dF}{dt}\cancel{t}$ can be very small. In this case, a fast unloading rate may be not necessary. The analysis above shows that equations (2.7) and (2.10) may be applicable to the spherical indentation of the viscoelastic-plastic materials. Now the key issue is how to accurately determine the projected contact area $A$ appeared in equation (2.8). This point will be addressed in detail below.

### 2.3.2 Effects of the Time-Dependent Deformation Behavior and the Plastic Deformation on the Determination of the Contact Area

In the OP method, the contact depth is determined from equation (2.8). Cheng et al.,\(^7\) point out that equation (2.8) is not applicable with or without the correction by Ngan et al.,\(^5\). Instead, they suggest using the simple correlation between the indentation depth, $h$, and the contact depth, $h_c$ (i.e., $h(t)=2h_c(t)$ for spherical indentation) to determine the contact area. However, this relation is only valid for the indentation of linearly viscoelastic materials and the ideal indenter geometries. When plastic deformation occurs or the indenter deviates from the ideal shape, the correlation used by Cheng et al.,\(^7\) may be invalid. Bearing this point in mind, we further examined the applicability of equation (2.8) using the material model given by fig. 2.1. The reason responsible for the inapplicability of equation (2.8) according to Cheng et al.,\(^8\) may be given as follows. In the indentation of time-independent materials, one-to-one relationship exists between the maximum indentation load and the depth in a single loading-unloading loop. However, in the indentation of time-dependent materials (e.g. polymers) the maximum indentation depth may correspond to different indentation loads depending on the loading rate and the holding segment for a displacement-controlled indentation (see fig. 7 in ref. 8). Thus, equation (2.8) does not give the unique contact area. In order to solve this problem, we may consider two extreme cases for the
indentation of viscoelastic plastic materials as given by fig.2.1. First, if the loading-unloading time is much shorter than the relaxation time, the material may behave like a time-independent elastoplastic material. The Young’s modulus of the material in this case represents the instantaneous modulus. Second, if both the loading and unloading rates are very slow, such that the loading and unloading segments are much longer than the relaxation time, the material may also behave like a rate-independent elastoplastic material. In this case, the Young’s modulus of the material can be regarded as the long-term modulus.

In the present study, the instantaneous modulus is the main concern; thus we will investigate the possibility to achieve the fast loading and fast unloading protocol corresponding to the first case. In equation (2.8), the initial unloading slope may be determined either from the fast unloading procedure or from equation (2.9) as proposed by Cheng et al., 7. In theory, well determination of the contact area by using equation (2.8) requires the use of the maximum indentation load corresponding to a sufficiently fast loading rate and the beginning point of the holding segment (if the holding segment is used). In the OP method, the maximum indentation load at the end of the holding segment is applied; this is incorrect in theory and may lead to significant errors. In practice, we face the question of how fast the loading rate should be. We make an attempt to answer this question by using the finite element analysis. Based on the computational results, it is found that when the loading time is much shorter than the relaxation time, e.g. $t_l < 0.1\tau$, the maximum indentation load at the beginning of the holding segment converges to a constant value (see fig. 2.6). Summarizing the analysis above, we suggest a protocol as illustrated by fig. 2.4 (a). The key issue in the protocol is that the maximum indentation load ($F_m$ in the figure) corresponding to the fast loading procedure and at the beginning point of the holding segment is used in the determination of the contact area. The initial unloading slope is determined from the unloading curve resulted by a fast unloading rate or equation (2.9). Using the protocol, the OP method may provide a good estimation on the instantaneous modulus of polymers. We verified this specific protocol by using numerical experiments. The
instantaneous modulus determined by using the protocol and equations (2.7) and (2.8) for the three sets of material parameters as given above are 2062MPa (Mat1), 2045MPa (Mat2) and 2041MPa (Mat3), respectively. Compared with the exact solution (2000MPa), it can be seen that, indeed, the OP method based on the protocol as identified above gives a quite reasonable evaluation of the instantaneous modulus. It is noted that many polymers have the relaxation time of tens or hundreds seconds, thus in practice it is possible to achieve the required fast loading condition by applying various commercialized indenters in the market. In theory, the fast loading procedure is not always necessary due to the plastic deformation. When the plastic deformation occurs, the extent of sinking-in of the indented material may be largely reduced. In this case, the ratio of $\frac{kF_m}{S}$ to $h_m$ (see equation (2.8)) can be very small; and the effects of the uncertainties in the maximum indentation load caused by the time-dependent deformation behavior of the materials may be negligible. The discussion above for the determination of the contact area focuses on the displacement-controlled indentation. For load controlled indentation, according to the analysis above, fast-loading procedure is also necessary for the well determination of the contact area. If a holding segment is used at the same time, the maximum load $F_m$ in fig.2.4 (b) estimated by extrapolation should be used in equation (2.7).

It has been noted that the indented material may exhibit piling-up when it undergoes plastic deformation. In this case, equation (2.8) shows that the OP method will underestimate the projected contact area and thus overestimate the reduced modulus. Hence, evaluating the applicability of equation (2.8) to viscoelastic-plastic materials requires a careful examination of the development of piling-up under the spherical indentation. For the spherical indentation of time-independent elastoplastic materials, it has been shown that the extent of piling-up depends on the materials properties and also the ratio of the indentation depth to the indenter radius $\frac{30}{\Phi_y}$. According to the computational results, the following information has been obtained. First, the larger the ratios of the indentation depth to the tip radius and $E_p$ to $\Phi_y$ are, the larger the ratios of the contact depth to the indentation depth will be. This
phenomenon is similar to that observed in the indentation of time-independent elastoplastic materials. Second, for the same ratios of the indentation depth to the tip radius and $E_p$ to $\Phi_y$, the larger the ratio of $E_p$ to $E_v$ is, the greater the ratio of the contact depth to the indentation depth will be. We have examined a critical case for which $E_p / \Phi_y = 100$, $E_p / E_v = 0.9$ and $h/R = 0.2$, the ratio of the contact depth to the indentation depth is smaller than 1.03; thus piling-up is indeed small, fig.2.7.

Fig. 2.6 Effect of the loading rate on the maximum indentation load (at a given indentation depth)

Fig. 2.7 Deformation of an indented material at the maximum indentation depth
2.4 SIMULATION OF THE INDENTATION CREEP TESTS BY USING THE VISCOELASTICPLASTIC MODEL

By using the OP method and the protocol suggested in this study, only the instantaneous modulus can be determined. Considering the limitations in the OP method, a number of novel methods have been proposed in recent years to determine the complete relaxation or compliance function from indentation tests (e.g. refs. 12, 15). The methods are mainly based on the elastic contact theories and the correspondence principle. When these methods are applied to polymers, the indented materials may undergo plastic deformation. Oyen pointed out that the examination of the shape of experimental load–displacement responses may be used to judge if appreciable plasticity occurs. In this work, we study the effects of the plastic deformation by using finite element simulations based on the viscoelastic-plastic model adopted in section 2. Based on the experience from the spherical indentation of the elastoplastic materials, the development of the plastic deformation in the indented viscoelastic-plastic solids will depend on the ratios of the indentation depth to the indenter radius. It is expected that the effects of plastic deformation on the performance of these new methods should be significant, when the ratios of the indentation depth to the indenter radius are greater than some critical values. Determination of such limits should be useful for the application of the novel methods to the viscoelastic-plastic soft matter.

We take method based on the indentation creep test as an example but the results may be instructive to other methods (e.g. the constant loading rate method). Using the indentation responses from the simulations, the instantaneous modulus and the long-term modulus have been determined by following the work of Oyen. One merit of this method is that it includes a ramp correction procedure. Briefly, the displacement – time (h–t) data were fitted to a function of the form,

\[ h^2 = b_0 - b_1 e^{-r_1} - b_2 e^{-r_2} \]  

(2.11)
where $b_0$, $b_1$, $b_2$, $\tau_1$ and $\tau_2$ are parameters. $E_0$ and $E_\infty$ are determined by

$$E_0 = \frac{2(1-\nu^2)}{(C_0 - C_1 - C_2)}$$

(2.12a)

$$E_\infty = \frac{2(1-\nu^2)}{C_0}$$

(2.12b)

where the parameters $C_0$, $C_1$, $C_2$ are given by

$$C_0 = \frac{b_0}{P_m F_g}$$

(2.13a)

$$C_1 = \frac{b_1}{P_m F_g R_{c,1}}$$

$$C_2 = \frac{b_2}{P_m F_g R_{c,2}}$$

(2.13b)

where

$$R_{c,1} = \frac{\tau_1}{t_r} \left( e^{\tau_1} - 1 \right)$$

$$R_{c,2} = \frac{\tau_2}{t_r} \left( e^{\tau_2} - 1 \right)$$

$$F_g = \frac{3}{8\sqrt{R}}$$

(2.14)

Where $t_r$ is the time when the indenter reaches the given indentation depth. $R_{c,1}$ and $R_{c,2}$ are ramp correction factors; and $F_g$ is the tip geometrical factor (see refs. 12 and 15 for detail). First, in order to highlight the effects of plastic deformation, for a material with $E_0 = E_v + E_p = 3.5$ GPa, $E_v/E_0 = 0.9$, $\nu = 0.4$ and $\Phi_f = 70$ MPa (the parameters are taken by referring to the properties of PMMA), the instantaneous modulus and the long-term modulus are determined. The results corresponding to different ratios of the $h_{\text{max}}$ to the indenter radius $R$ are given in fig. 2.8, where $h_{\text{max}}$ is the maximum indentation depth at which the creep test stops. Fig. 2.8 shows that when the ratios of the indentation depth to the indenter radius is larger than 0.012, the errors in $E_0$ and $E_\infty$ will be greater than 10%. In fact, when $h_{\text{max}}/R = 0.006$, plastic deformation already becomes significant, but its effects are small. In the sequel, we will make an attempt to determine the critical ratios of $h_{\text{max}}/R$ beyond which the effects of plastic deformation are significant. In the simulations, the ratio of $E_p/E_0$ varies from 0.1 to 0.9 and $\Phi_f/E_p$ are in the range of 0.01 to 0.1. For a given set of material properties, $h_{\text{max}}/R$ will be varied in a wide range. A total of around 100 simulations have been undertaken. The critical ratio $h_{\text{max}}/R$ are
determined below which the errors in $E_0$ and $E_\infty$ caused by the effects of plastic deformation are smaller than 10%. It is found from the computational results, that for the same ratio of $\Phi_y/E_p$, the larger the ratio of $E_p/E_0$ is, the smaller the critical ratio of $h_{max}/R$ will be. Thus, it is sufficient to use the results corresponding to the large ratio of $E_p/E_0$ to determine critical ratio of $h_{max}/R$ below which the effects of plastic deformation is small. In this case, we report the critical ratio of $h_{max}/R$ corresponding to different $\Phi_y/E_p$ and for $E_p/E_0=0.9$ (circle points and the solid line in fig. 2.9). The triangle points represent the results corresponding to $E_p/E_0=0.1$. By using the results proposed herein and some prior knowledge about the ratio of $\Phi_y/E_p$, one can estimate the proper ratios of $h_{max}$ to $R$ to ease the effects of plastic deformation when setting up the experiments. For example, for the polymers used in the experiments of Tranchida et al.,\(^9\) (polycarbonate (PC), polystyrene (PS), polyethylene terephthalate (PET), isotatic polypropylene (iPP)), they stated that the ratio of modulus to the yield strength are in the range of 30~37. If the spherical indentation creep tests\(^{15}\) are performed on these polymers, it is proper to control the ratio of $h_{max}/R$ below 2% according to fig. 2.9, in order to make the plastic deformation effects negligible.

![Graph](image1.png)

Fig. 2.8 Dependence of the identified moduli on the ratio of $h_{max}/R$ due to the effects of plastic deformation
2.5 CONCLUSIONS

A number of fundamental issues regarding the spherical indentation of viscoelastic-plastic soft matter are examined via finite element analysis based on a viscoelastic plastic model. In summary, the following contributions have been made. First, using finite element analysis based on a viscoelastic-plastic model, the two fundamental relations in the OP method are examined. The analysis shows that the correlation between the initial unloading slope, reduced modulus and the projected contact area (equation (2.7)) may hold true even the indented material undergoes viscoelastic and plastic deformation simultaneously. The condition is that the contact stiffness should be determined by using the fast unloading protocol or corrected by following the procedures reported by Ngan et al.,\(^5,6\) or Cheng et al.,\(^8\). Recently, Cheng et al.,\(^8\) showed that equation (2.9) with or without the correction of Ngan et al.,\(^5,6\) is inapplicable to the indentation of viscoelastic materials. The present study shows that such a failure may be overcome by using the fast loading procedure and appropriate maximum indentation load as shown in fig. 2.4. Using such a protocol, the OP method may still applicable to the indentation of viscoelastic or viscoelastic-plastic materials. Second, using finite
element simulations based on the viscoelastic-plastic model, we studied the effects of plastic deformation on the indentation creep tests \(^{15}\) in determining the viscoelastic properties of polymers. The analysis suggests the critical ratios of the maximum indentation depth to the indenter radius for a wide range of property range, beyond which the effects of plastic deformation are significant. Although the results are proposed for the method based on indentation creep tests, they might be instructive to the methods based on the constant loading rate tests \(^{9}\).

References:

8. Y. T. Cheng, W. Y. Ni, C. M. Cheng: Determining the instantaneous modulus of


21. N. Huber, E. Tyulyukovskiy, Schneider H. C., Rolli R., Weick M. An indentation system for determination of viscoplastic stress-strain behavior of small metal


CHAPTER 3

3. EXPERIMENTAL RESULTS

3.1 NANOINDENTATION OF POLYMERS

The current developments in fields such as nanoimprints, BIOMEMS (Bio-Micro-Electro-Mechanical-Systems) devices, coatings, biological materials, and nanocomposites demands more precise knowledge of the mechanical properties of polymers at the nanometer length scale. Few means exist to experimentally measure and verify key mechanical properties of polymers confined to small volumes. The most widely used characterization technique in that field is nanoindentation, which can be used to evaluate quasi-static mechanical properties of materials confined to small volume like the reduced Young’s modulus and the hardness. Many investigations have used nanoindentation tests to study mechanical properties, like fracture toughness, adhesion, creep, extracting stress vs strain curves, of metallic and polymer films. Furthermore, some examples of characterizing different polymers, relating microstructure to mechanical properties, and processing conditions are discussed below. Van Landingham et al. investigated the dependence of the nanoindentation response on the crosslink density of cured epoxy, poly methyl metha acrylate (PMMA), and polydimethylsiloxane (PDMS), both in quasistatic and dynamic conditions. Boersma et al. had shown the capability of load and depth-sensing indentation to evaluate the effect of physical and chemical aging on polycarbonate (PC) coatings. Flores et al. investigated microhardness on chain-extended polyethylene (PE), deepening the correlation with microstructure, creep behavior and temperature, yield stress and elastic modulus. Meijer and Govaert performed a study to understand the intrinsic deformation behavior of polymeric materials relating to the molecular structure of polymers. Suwanprateeb performed a study on high density polyethylene (HDPE) to evaluate the effect of annealing conditions. The same author had also studied the different methods for determining load and time dependence of Vickers hardness in
PMMA and PE. Shen et al., used nanoindentation for investigating the mechanical properties of clay nanocomposites to identify the effect of clay loading and strain rate. They chose a three-side pyramid indenter (Berkovich) for experimentation, and this configuration is probably the most widely used in recent nanoindentation studies.

For polymers extracting properties are intrinsically limited because it attempts to derive a quasi-static quantity from a time-dependent material. Therefore, knowledge of creep and sensitivity of various experimental variables are important parameters for extracting the correct properties without overestimations. Bricose et al., proposed compliance method to measure the microhardness of a number of polymers. It has been shown that this method is reliable and consistent in comparison with the conventional residual imaging technique. The compliance curve provides the hardness, a plastic yield characteristic, and the Young’s modulus for the material. Creep of polymers was studied by nanoindentation for a variety of polymers, above and below their glass transition temperatures, and correlated with their molecular mobility. An extensive study to predict the creep rate as a function of the loading rate and the maximum load was carried out. Oyen performed nanoindentation with a range of conditions including different load levels and ramp times to examine the sensitivity of experimental variables. Dub and Trunov performed studies on viscoelastic solids to determine the viscosity and relaxation time from experiments on step-loading nanoindentation. Tweedie combined instrumented indentation and SPM (Scanning Probe Microscopy) imaging to demonstrate the post-indentation viscoelastic recovery with simple linear models. Summarizing the main efforts from all the mentioned studies, indentation is a suitable technique for polymer characterization. However, the widely used analysis method (Oliver and Pharr) has serious issues while characterizing polymer. The inherent time dependence of polymer mechanics (viscoelasticity), creep, pileup, surface forces, interferes with the results and invalidates the OP method. Although the OP method has been successfully used to determine the Young’s modulus and the hardness of metallic materials, ceramics, but the failure of
the method has been frequently reported in recent years when it is applied to the characterization of polymers\textsuperscript{33-36}. Many researchers have proposed various models and phenomenological correction factor for measuring viscoelastic solids with prominent time dependence\textsuperscript{35}. Tranchida et.al\textsuperscript{33}, have reported that the contact mechanics from the Oliver & Pharr analysis method is based on elastic solution which cannot be applied for cases where viscoelasticity is observed. A theoretical investigation on the applicability of the OP method has been performed in chapter 2 by using numerical simulations based on a viscoelastic-plastic model; the results show that the OP method may still work well provided an experimental protocol as identified can be followed. In the present chapter, experiments performed on four different polymers by using a 5µm radius spherical tip to validate the findings obtained from the computational modeling.

In order to consider the strain and strain-rate dependence of polymers, experiments were performed for a range of strains using a spherical geometry indenter. This geometry allows one to test the polymers from low strains (viscoelastic) to high strains (viscoelastic-plastic). The experimental procedure, results, and corresponding analysis are provided below in detail.

\section*{3.2 Preliminary Characterisation}

In depth sensing indentation (DSI) the load and depth of penetration are directly measured during loading and unloading of the indenter using which the elastic modulus and the hardness are calculated. In practice various errors are associated with this procedure. The most serious of these errors manifests themselves as offsets to the depth measurements, others from environmental changes during the test, non-ideal shape of the indenter and the surface roughness of the sample. There are few basic issues to be considered while mechanically characterizing a material by DSI especially when properties are probed in nm range. They are local surface roughness of the testing material, knowledge about the tip geometry, machine compliance, initial contact point and, thermal drift.
3.2.1 SURFACE ROUGHNESS

Surface roughness is an important issue in nanoindentation at lower depths it influences the results from instrumented measurements. The surface asperities decrease the mean contact pressure by increasing the contact radius. Thus for a given indentation load, depth of penetration is reduced and the computed modulus is also reduced. The roughness parameter ($\alpha$) increases with radius of the indenter, and $\alpha$ increase with decreasing indentation load.

$$\alpha = \frac{\sigma_s R}{a_0^2}$$  \hspace{1cm} (3.1)

In equation (3.1) $\sigma_s$, R, and $a_0^2$ are maximum asperities height, indenter radius and the contact radius respectively. Thus for low loads with spherical indenter, surface roughness can have significant effect \(^{37}\). Local surface roughness were measured using AFM (atomic force microscopy) (Veeco Metrology Group, Dimension \(^TM\) 3100) for both calibrating and testing materials. The local roughness values were a maximum of 12nm for quartz and about 2nm for most of the polymers. The surface profile for PMMA with a scan size of 10µm x 10µm, and 2D profile for PET are exemplarily shown in fig.3.1.

Fig.3.1a AFM surface profile with 10µm x 10µm scan size - PMMA.
3.2 TIP DEFECTS AND CALIBRATION

Tip defects, which are always present due to technological limitation in the manufacture of the indenter, may greatly affect the evaluation of the mechanical
properties of the materials. They were always a problem in measuring the properties especially when material is probed in nanometer range. This generic error may be corrected to some extent by using the magnified images of indenter profile. We used a 5µm and 1µm spherical indenters to measure the modulus and hardness for all polymers. Field Emission Scanning Electron Microscope (FE-SEM, LEO 1550VP, GEMINI) images were made to map the tip radius, and tip irregularities fig. 3.2a. Furthermore to obtain the three dimensional view of the indenters, it was rotated in different degree of observation under SEM from $0^0$ to $360^0$ to identify the tip defects and irregularities. From the FE-SEM images, the tip radius was estimated as 5.3µm for 5µm spherical indenter and no dominant tip irregularities is observed, fig.3.2b. In the case of 1µm spherical indenter we observed a wavy geometry and a non-axisymmetric structure at the tip apex instead of a spherical geometry, fig. 3.3. This behaviour is observed approximately upto 100nm from tip apex. The probing depth range is from 5 to 200nm for all performed experiments. The occurrence of tip defects is in a crucial depth range in comparison with the probing depth.

![5µm spherical indenter](image)

Fig.3.3b SEM image of the indenter used to calculate the tip radius.
The general procedure followed for calibrating the tip as proposed by Oliver and Pharr results in an area function to overcome the issue of serious tip defects. The area function describing the real indenter profile used for indentation experiments requires a precise calibration, especially when taking tip imperfections or irregularities into consideration. The calibration procedure was similar as described elsewhere \cite{32, 37-38}, and a brief discussion are provided herein. The procedure requires using a standard material with uniform and well-known material properties (especially the Young’s modulus, eg. quartz) for determining the area function. We had the following difficulties in using quartz as a calibration material. First, it had a relatively high surface roughness (12nm) in comparison to the indentation depth. Second, the maximum indentation depth with the Triboscope was only 100nm for quartz, and reaching higher depths causes instability in the force transducer. For this reasons, we used PMMA as a calibration material.

Fig.3.3 SEM image of the indenter with tip defects at different angles of observation.
Furthermore recently several reports have reported that a polymer has to be used as a calibrating material in using OP method and PC was used in most cases\textsuperscript{33, 36}. Moreover, for PMMA the influence of the surface energy on the contact area is almost negligible which are discussed in chapter 4. For these reasons PMMA is used as a calibrating standard with well known material properties. The area-function was determined for a contact depth ranging from 5nm to 300nm. The calibration was repeated several times and no significant change in the area function was observed.

\subsection{3.2.3 INITIAL CONTACT POINT}

In the following we will describe the different methods of sample surface finding. The first possibility is the definition of a pre-set load value, at which the loading and unloading process starts and displacement values are set to zero. The pre-load is accounted for as part of the load on the surface, but the corresponding penetration into the surface is neglected, thus introducing an error in the calculation of the contact depth and area. The higher the pre-load value, the bigger the underestimation of the contact area and thus the overestimation of hardness and modulus values tends to be. A second way of identifying contact formation between the tip and the sample is monitoring the slope in the load - displacement plots, i.e. the slope of the secant $\Delta P / \Delta h$ in units of N/m. In our experiments the first method is used for surface detection\textsuperscript{40}.

\subsection{3.2.4 THERMAL DRIFT}

There are two types of drift behaviour that might be observed in Nanoindentation testing. First is the creep within the specimen material as the result of plastic flow. Another is the change in dimension of the instrument due to thermal expansion or contraction of the apparatus. This change in depth imposes a thermal drift error into the real depth of penetration. Feng and Ngan\textsuperscript{41} undertook a detailed study on the effect of thermal drift to determine under what conditions it would have a negligible effect on
the computed value of elastic modulus, equation (3.2). They found that \( t_h \) is the total time from the start of the test to the beginning of the unloading, then it shows that the thermal drift has minimum effect on the computed elastic modulus if,

\[
t_h = \frac{h_p S}{P|_0}
\]

where \( S \), \( |P|_0 \) and \( h_p \) are the contact stiffness, unloading rate and the contact depth.

### 3.2.5 MACHINE COMPLIANCE

The depth of penetration of the indenter into the specimen and also any displacement of the instrument arising from reaction forces during loading. The uncertainties in the load frame compliance is directly proportional to load, and the affects the measured modulus at higher loads which is negligible for polymer 42.

### 3.3 INDENTATION PROCEDURE

Nanomechanical characterization is performed for all polymers with a Hysitron Triboscope (Hysitron Inc.). The Triboscope can be operated in both open and closed loop feedback system, which controls the load applied to the indenter by means of an electrostatic transducer 42. The difference between feedback controls is that complete separation between the load and displacement measuring system is possible in closed loop system which is not in another case. The theoretical depth resolution of Triboscope is in sub-nanometer range. Instrument compliance was calibrated on quartz. The maximum thermal drift was 0.027nm/s before starting the indentation. Drift correction was used to minimize thermal effects. The zero point load or intial contact force is the force used by the indenter to identify the sample surface. The initial contact load of 0.5µN was used which is the smallest possible force with Triboscope 42. A spherical indenter with a 5µm tip radius is applied. We performed indents on polymers using the
closed loop, displacement control mode from 5nm to 200nm. The protocol as suggested by the computational studies is used, fig.3.4. Each indent was made using a trapezoidal loading function in which the indentation depth was first increased to the maximum set value and then held at the peak value before unloading. In each case, an array of ten indents at five different places was made for all chosen polymers. All the experiments were performed at room temperature.

Fig. 3.4 A schematic of the loading-holding-unloading protocol suggested in the present study - displacement-controlled instrument.

3.4 MATERIALS STUDIED

In order to validate the findings from chapter 2, polymers exhibiting different mechanical properties are studied ranging from amorphous to semi-crystalline structure and from glassy to rubbery mechanical behaviour. The adhesion energy between the indenter and the sample varies significantly between polymers so that we can study the effect of adhesion in determining the modulus and verify the theoretical analysis performed in chapter 4. Four different polymers are investigated i.e., low-density polyethylene (LDPE), polystyrene (PS), polyethylene terephthalate (PET), and
polypropylene (PP) (GoodFellow, refer appendix)\textsuperscript{43}. The polymers were mechanically homogenous as verified by microindentation (Fischerscope).

3.5 GENERAL CHARACTERISTICS OF THE CHOSEN POLYMERS USING INDENTATION

3.5.1 INTRINSIC DEFORMATION BEHAVIOUR

Intrinsic deformation is defined as the material’s true stress-strain response during homogeneous deformation. Although details of the intrinsic response differ per material, a general representation of the intrinsic deformation of polymers can be recognized, see figure 3.5.

![Intrinsic Deformation Behaviour](image)

Figure 3.5 Schematic representation of the intrinsic deformation behaviour of a polymer material.\textsuperscript{44}

Initially we find a viscoelastic, time-dependent, response that is considered to be fully reversible. For small loads the material behaviour is linear viscoelastic, while with increasing load the behaviour becomes progressively nonlinear. At the yield point the deformation becomes irrecoverable since stress-induced plastic flow sets in leading to a
structural evolution which reduces the material’s resistance to plastic flow: strain softening. Finally, with increasing deformation, molecules become oriented which gives rise to a subsequent increase of stress at large deformations: strain hardening

Independent of the stress level or amount of deformation involved, the origin of the deformation of polymers lies in their ability to adjust their chain conformation on a molecular level by rotation around single covalent bonds in the main chain. This freedom of rotation is, however, controlled by intramolecular (chain stiffness) and intermolecular (inter-chain) interactions. Together these interactions give rise to an energy barrier that restricts conformational changes of the main chain. The rate of conformational changes, i.e. the molecular mobility, is determined totally by the energy available in the system. Molecular mobility is determined by the molecular energy, which is constant for a given temperature. Under a small constant load or deformation (linear range) this mobility gives rise to pronounced time dependence, as illustrated schematically in fig.3.6. The behaviour is governed by two characteristic relaxation mechanisms: the glass transition and the reptation process. On short time scales the response is solid-like since only limited molecular rearrangements are possible. With increasing (logarithmic) time scale or strain levels, the size of the conformational
changes increases, ultimately resulting in unbounded segmental diffusion at the glass-rubber transition. Large scale motion of polymer chains is however, inhibited by physical entanglements that can be envisaged as temporary cross-links. At this stage the polymer effectively behaves like a rubber, whereas at even longer times, reptation enables main-chain diffusion (entanglements are dissolved), and the polymer behaves as a fluid (melt)\textsuperscript{44}. In our study we choose polymers with different mechanical behaviour viz: rubbery and glassy. In the following section we will discuss the sensitivity of the experiments in differentiating the mechanical behaviour between polymers.

A case study is performed in this section considering the force-displacement response for different materials. The maximum depth of 100nm is considered as an example for discussion. The differences in hardness of materials are apparent from the large differences in the maximum force reached for a maximum depth, fig.3.7. The softest material is LDPE to reach a maximum depth (~ 100 nm) a force of 25µN is used, while the harder PS needed a force of 100µN. PMMA, PET and PS show a similar response with relatively similar hardness. Most of the indenter displacement in all polymers is elastically recovered on unloading. But they show various degrees of elastic recovery the largest being LDPE. PP is the case where the maximum plastic deformation in the material has taken place, fig.3.11.
Fig. 3.7 Force-displacement at a depth of about 100 nm for different polymers is shown.
Contact stiffness is another source which provides information about the material property and moreover it is the parameter used in Oliver and Pharr analysis method to extract material parameters. A plot between contact stiffness and contact depth can provide information in terms of material behaviour. It is possible to differentiate between the two mechanical behaviour the rubbery and glassy from the plots. This difference can be also due to the lower modulus of the rubbery when compared to glassy mechanical behaviour of polymers. This observation is noted independent of the indenter geometry, which explains the difference in mechanical behaviour is observed irrespective of the strain levels (from indenter geometry). The spherical indenter is used for lower and berkovich geometry for higher strain levels. Another interesting comment on this plot is that, the difference in microstructure is not observed. Moreover in the case of the spherical geometry (conospherical tips) indenter tips are with spherical ends with a cone angle of 60 degrees. Furthermore, in fig.3.8 the transition from the spherical to conical geometry is gradual which is noted from changing slope. There exists a theoretical critical depth vertical distance \( h^* \) from the tip apex, such that below which the probe can be modeled as an ideal sphere of radius \( R \), and above \( h^* \), only \( \theta \) defines the increase in contact area with distance, equation (3.3)\(^{45}\).

\[
\frac{h^*}{R} = 1 - \sin \theta
\]  

(3.3)

This critical depth for spherical indenter of 5µm radius and 60\(^0\) cone angle is approximately 670nm; whereas for berkovich geometry with approximated cone angle (70.3\(^0\)) with 200nm tip radius is 12nm. For the conical tips, we observe almost linear relationship between the contact stiffness and the plastic depth (see fig.3.8) as expected when the conical part of the tip goes in contact with the material. In the case of berkovich geometry only the linear part of the slope is noticed in the stiffness vs depth plot reflecting the geometry, fig.3.9.
Fig. 3.8 Stiffness-contact depth plot for various polymers obtained using the spherical indenter.

Fig. 3.9 Stiffness-contact depth plot for various polymers obtained using the berkovich indenter.
3.6 VALIDATING THE RESULTS FROM COMPUTATIONAL STUDY WITH EXPERIMENTS

The experimental protocol developed in chapter 2 is validated experimentally in this section and is based on two considerations. 1) The consistency of the procedure is studied with respect to the nature of soft matter. 2) The instantaneous modulus for polymers is examined at different deformation regimes to examine consistency.

3.6.1 DETERMINATION OF THE INSTANTANEOUS MODULUS BY USING A SPHERICAL INDENTER

Polymers reveal strong strain and strain-rate dependent properties and show different mechanical response under different contact conditions. The experimental time scale for viscoelastic solids influences the modulus to be either the instantaneous or the long-term modulus. The aim of the current experimental procedure is to yield the instantaneous modulus. A trapezoidal loading procedure was used consisting of the three segments loading, holding, and unloading. The loading rate is an important criterion for viscoelastic solids. This means that the force required in reaching a given indentation depth increases with the loading rate and converges at higher loading rates. If sufficiently fast loading rates is not achieved, then the maximum force corresponding to maximum depth is different for different loading rates as shown in figs. 3.10a, 3.10b for PS, and LDPE. To obtain a sufficiently fast loading rate, loading segment times of 0.5s, 5s and 50s are tested. Thus, for the same indentation depth the lower the segment time is, the faster the loading rate will be. A loading segment time of 50s was not sufficient for both rubbery and glassy polymers to obtain convergence as shown in figs. 3.10a, 3.10b. To achieve sufficiently fast loading or unloading rates the total segment time should be 0.1 to 0.01 times the relaxation time for polymers. For PET and PS with loading segment time of 5s, a sufficient loading condition was obtained; whereas for LDPE and PP it was 0.5s. A holding segment becomes necessary to avoid the...
initial negative slope, as shown in fig. 3.10c for LDPE with 0s and 10s holding time\textsuperscript{36, 46}. Simulations in chapter 2 also suggest that the use of longer holding time may not require very fast unloading rates. The fastest possible unloading segment time of 0.5s is applied \textsuperscript{47}. The unloading rate was fast enough so that the overshoot\textsuperscript{1} disappears and the unloading slope converges to elasticity. All the above discussions related to loading, holding, and unloading conditions are shown in fig. 3.10 for both rubbery (e.g. LDPE) and glassy (e.g. PS) polymers. The conditions used for attaining the instantaneous modulus were a loading segment time of 0.5s or 5s, holding time of 10s, and unloading segment time of 0.5s, respectively, fig. 3.10d. The force-displacement response for PET and PP satisfying these conditions is shown in fig. 3.11. The obtained reduced modulus is the instantaneous modulus for PP, PS, PET, and LDPE, fig3.11.

\textsuperscript{1}Overshoot - The ‘nose’ that appears at the end of loading segment for viscoelastic solids leads to a negative slope when calculating the stiffness.
We can classify the tested polymers based on their relaxation time or mechanical behaviour. Fig. 3.10 compares the mechanical response for glassy and rubbery polymers at similar depths using PS and LDPE, respectively. Rubbery polymers with lower relaxation time (PP and LDPE) require faster loading rates, whereas glassy polymers (PS and PET) require slower rates to yield sufficient loading conditions, fig. 3.10a, 3.10b. The experimental protocol, with a loading time, holding time and unloading time for PET and PS was 5s, 10s, and 0.5s respectively; whereas for LDPE and PP was 0.5s, 10s, and 0.5s respectively was used in obtaining the instantaneous modulus, fig.3.11. The observed loading rate dependence is the strain rate dependence of polymers, and it was found to be stronger for the tested rubbery polymers than for the glassy polymers. The experiments show that selecting a sufficiently fast loading and unloading rate in

![Figure 3.10c](image_url)  
**Fig. 3.10c** LDPE - A hold segment avoids the initial negative slope.

![Figure 3.10d](image_url)  
**Fig. 3.10d** The convergent loading, a hold, and a fast unloading are shown for rubbery (LDPE) & glassy (PS).

Fig.3.10 Further examination of the experimental results was performed as explained above to satisfy the theoretical conditions (chapter 2) in order to achieve the instantaneous modulus.
conjunction with an appropriate holding segment may efficiently reduce the data scatter in obtaining the instantaneous modulus.

**Fig. 3.11** Force - displacement for PET & PP (strong strain rate dependence while loading).

**Fig. 3.12** Instantaneous (reduced) modulus for glassy and rubbery polymers. The error bar represents the different values obtained for the reduced modulus at the same depth.

### 3.6.2 PROBING PROPERTIES ACROSS THE DEFORMATION REGIME

A spherical indenter with radius ‘R’ (5µm) is indented in a viscoelastic solid. The ratio of contact depth to contact radius increases with depth of penetration (geometrically non-similar). The characteristic strain ($\varepsilon_{rep}$) also increases with depth of
penetration given by equation (3.4), where \( a \) is the contact radius.

\[
\varepsilon_{\text{rep}} = 0.2 \frac{a}{R}
\]  

(3.4)

With the spherical indenter, the deformation is initially elastic with increasing \( \varepsilon_{\text{rep}} \) the deformation regime is shifted to elastic-plastic and finally results in plastic flow. In the transition between linear viscoelastic to viscoplastic, the mode of deformation is one of radial expansion caused by hydrostatic stress beneath the indenter.\(^{48}\) Using spherical indenter avails the possibility for characterizing the strain dependent property of polymer at different deformation regimes viz., linear viscoelastic, viscoelastic and viscoelastic-plastic. Linear viscoelastic solid (much > T_g) when load is applied the deformation is instantaneous, after which it remains constant until the load is removed, where the recovery is instantaneous and complete. For a single loading process the stress and strain are linearly proportional. In viscoelastic regime the total strain is sum of immediate elastic deformation, delayed elastic deformation and Newtonian flow. This regime is characterized by retardation time of the polymer. Furthermore scanning to higher load end, polymer undergoes viscoelastic-plastic deformation involving permanent set or rejuvenation. The basic deformation governing mechanism has changed from secondary (segmental mobility) to primary deformation involving main chain or back bone contributions.

In all the tested deformation limits it is possible to measure material property by a well defined experimental protocol as discussed above. In all the tested strain limits consistent material property or the instantaneous modulus are obtained. Consistent data for different deformation regimes and for different polymers (glassy or rubbery polymer) are obtained. Until this stage we are able to produce an elastic relaxation during unloading resulting in a consistent reduced modulus and hardness. It is obvious from the obtained results that, even in viscoelastic regime we could avoid the viscoelastic relaxation effects which affect the stiffness measurements. These results
prove that a properly designed experimental protocol can be used to measure the bulk mechanical properties for viscoelastic solids irrespective of their corresponding microstructure using a spherical indenter. It is not possible to clearly differentiate between different deformation regimes, but the mechanical hysteresis observed at different indentation depth are different, and this could be due to the transition occurring between regimes, fig. 3.12. It is noted from the force-displacement curves transition occurring between regimes and the creep or bulge at the end of the unloading segment. In spite of these reasons a consistent material properties are obtained in all the tested regimes.

![Force - displacement curves from viscoelastic to viscoelastic-plastic limits for PET.](image)

**3.6.2 CORRECTING THE MAXIMUM LOAD**

Viscoelastic behaviour can be seen as an increase in penetration depth when the load is constant. This actually becomes a problem while analyzing the data via
displacement control (DC). Using a holding segment avoids the overshoot from the viscoelastic flow in the unloading slope but it simultaneously creates an error in retrieving the maximum load ($P_m$) which in turn is required in eqs. (2), (3). The maximum load ($P_{actmax}$) appearing at the beginning of the holding segment is used in our analysis (fig. 3.13). The analysis was hence carried out in such a way that we extracted $P_{actmax}$, stiffness, and $h_m$ from the force-displacement curve using an area-function for calculating the reduced modulus. The instantaneous modulus from this non-standard analysis was compared to the OP method, to give an estimate of the error that may occur when using a standard OP analysis. To make a valid comparison for $E_r$ we used data beyond the critical depth (30nm) to avoid the influence of surface forces, fig. 3.14. Details about the critical depth are discussed in section 4. An error of 10% was noticed in the reduced modulus when using the standard OP method for depths around 40nm. This error decays exponentially at depths of about 100nm for both glassy and rubber polymers. These results clarify that in the viscoelastic deformation regime an improper use of $P_m$ affects $h_c$ in eq. (2.8) which alters $E_r$ in eq. (2.7). At greater depths, polymers undergo plastic deformation so that the effect of the ratio $P_m/S$ on the contact depth is negligible. Thus, we observed that plastic deformation might be an advantage when estimating the reduced modulus of viscoelastic-plastic solids.

![Graph](image)

**Fig.3.14** The underestimation of actual maximum load for viscoelastic solids in displacement controlled mode.
Chapter 2 of this study introduced that the Oliver & Pharr (OP) method may be applied to the characterization of viscoelastic-plastic materials by using an improved experimental protocol. In this chapter, this finding was validated using four different polymers by nanoindentation experiments. The reduced modulus obtained for all polymers using the improved protocol is consistent with values reported in the literature. The study shows, that it is possible to use the OP method in conjunction with an improved protocol to characterize the nanomechanical properties of soft matter. Consistent material property or instantaneous modulus values are obtained for different deformation regimes independent of the nature of the polymer using the improved protocol.

Fig. 3.15 The reduced modulus calculated from the coded program considering the actual maximum load in displacement controlled mode in analysis for 1µm spherical indenter.

3.7 CONCLUSIONS
protocol. The results in this study may be applied to characterize soft matter including polymers and biological materials by nanoindentation.

**Suggested improved experimental protocol:**

- Characterization of the polymer and indenter geometry
  - Polymer – local surface roughness measurements (AFM)
  - Indenter geometry – tip defects and the tip radius (SEM)
- We recommend calculating the modulus and hardness for polymers using blunt/spherical indenters without serious tip defects. The case of the pyramidal geometry was not studied in this work.
- A trapezoidal loading procedure with a sufficiently fast loading and unloading rate in conjunction with an appropriate holding segment should be used.
- For viscoelastic solids, care should be taken when using displacement control (DC) in choosing the actual maximum load $P_m$.
- We recommend performing indents over a range of different depths to identify the critical depth. This is required in order to retrieve the actual modulus and the hardness values using the standard OP method.

**REFERENCES**


CHAPTER 4

4. INFLUENCE OF SURFACE ENERGY

4.1 SURFACE FORCES

It is well established that there are four distinct forces in nature. Two of these are strong and weak interactions that act between neutrons, protons, electrons and other elementary particles which have a very short range of action. The other two forces are electromagnetic and gravitational interactions that act between atoms and molecules. These forces are effective over a much larger range of distances, from sub-atomic, to practically infinite distances. The nature of surface forces of our interest is the van der Waals originating from electrostatic (electromagnetic) interactions involving charges or dipole molecules. These forces have been variously known as dispersive forces, London forces, charge fluctuations forces, electrodynamic forces and induced dipole-induced dipole forces. Dispersive forces are the most important contributions to the total van der Waals force between atoms and molecules. They play role in host important phenomena such as adhesion, surface tension, physical adsorption, the properties of gases and liquids, the strength of solids, the structure of condensed macromolecules such as proteins and polymers. Dispersive forces are of long range order can be effective from large distances to interatomic spacing. They can be attractive or repulsive and forces between molecules and do not follow a simple power law because the interaction of two bodies is affected by the presence of other bodies near by (non-addactive interaction). There is no general equation for describing the interaction between molecules and their distance dependence. Instead, an empirical potential function is used. The most common of such potentials are the hard sphere potentials, the inverse power law potential and the exponential potential. If atoms are considered as hard spheres, the repulsive force suddenly becomes infinite at certain interatomic separation. The radius of an atom or molecule is called as hard sphere or van der Waals
pack radius, fig.4.1.a. The other potentials are more realistic in that they allow for finite compressibility or softness of atoms, fig.4.1.b and the exponential potential is generally recognized. The best known of these potentials is the Lennard-Jones or ‘6-12’ potential. The repulsive and the van der Waals potentials are the first and second term in equation 4.1 respectively. The repulsive term decreases the strength of binding energy at equilibrium by 50%. This is compared to the hard sphere repulsion potential where binding energy at equilibrium would be just the van der Waals energy.

\[
W(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]
\]  

(4.1)

The van der Waals energy between atoms and molecules is of short range having an inverse sixth power distance dependence, but that between large condensed bodies decays much more slowly with distance \((1/r)\) for spheres and \((1/r^2)\) for planar surfaces and is effective for much longer range.

4.2 THEORITICAL MODELS

The problem of contact and adherence of spheres has a long history. Mechanics of contact, surface physics and fracture mechanics are mixed in an intricate manner. Assuming an elliptical distribution of pressure in the contact area, Hertz \(^2\) (1882) established his famous theory. Later Griffith made a breakthrough by coupling elasticity and surface energy (\(\gamma\)) in his famous theory; to extend the area of crack \(dA\), the work
2γdA is needed. Johnson–Kendall–Roberts\(^3\) (JKR) model is based upon Griffith theory, a balance of potential, elastic and surface energy predicted that equilibrium area of contact is larger than the Hertz theory. In the absence of molecular forces, the Hertz model has been shown to accurately describe the contact area between elastic spheres, fig.4.2. Adhesive forces arising from attractive surface forces are not negligible at small scales and must be included in any description of contact area. The critical pull-off force \(F_{JKR}\) at zero loads is given by equation 4.2,

\[
F_{JKR} = \frac{3\pi wR}{2}
\]

Derjaguin et al presented a completely different theory namely Derjaguin–Muller–Toporov\(^4\) (DMT) model assumed that the attractive forces do not change the form of the particle corresponding to the solution of Hertz problem. They assumed molecular forces act in a ring shaped zone of non contact adhesion, and can be defined by the equation of Hertz theory. They used a thermodynamic approach where the attractive forces outside the contact add a fictitious load which decreases from \(2\pi wR\) to \(\pi wR\) when the approach increases, whereas in the force method this fictitious load
increases continuously from $2\pi w R$. The critical pull-off force $F_{DMT}$ at zero loads is given by equation 4.3,

$$F_{DMT} = 2\pi w R$$ \hspace{1cm} (4.3)

In JKR approximation, adhesion forces outside the area of contact are negligible and elastic stresses at the edge of the contact are infinite. On the other hand, in the DMT approximation the adhesion forces are taken into account, but the profile is assumed to be Hertz, as if adhesion forces could not deform the surface. A long dispute began when Tabor \footnote{5} compared the two theories and pointed out the drawbacks in DMT theory is the neglect of the deformation due to attractive forces close to edge of contact. On the other hand, sharp discontinuity of displacement in JKR theory under zero loads occurs when the height of the ‘neck’ around the contact zone becomes comparable to the equilibrium separation $Z_0$ between atoms. In this case JKR theory must be corrected to take into account the forces outside the contact zone. Thus the tabor defined a transition parameter $\mu$ which sets the working limit for JKR and DMT theories and is given by equation 4.4.

$$\mu = \left( \frac{R \chi^2}{E_r z_0^3} \right)^{1/3}$$ \hspace{1cm} (4.4)

Here $R$, $E_r$, $\chi$ are the indenter radius, reduced modulus and the adhesion energy between the contact surfaces, respectively. The quantity $\mu$ is in fact equal to the ratio of the elastic deformation just before the surface separate to the equilibrium separation. JKR theory is generally used for cases with strong adhesion forces and larger tip radii and DMT in the opposite limits for stiff material, weak adhesion forces and smaller tip radii. Figure 4.3 compares the Hertz, JKR, and DMT with the realistic interaction, and a graph plotted vs contact area/$\pi$ and load for different approximations, fig.4.4.
Fig. 4.3 Interaction forces for Hertz, JKR, and DMT models, compared to a realistic interaction. There is no interaction force in the Hertz model, only hard wall repulsion at contact. JKR includes for short range and DMT for long-range surface forces. For an actual interaction force, the integral of the force-distance attraction well corresponds to the work of adhesion.

Fig. 4.4 The Hertz area-load curve and the JKR-DMT transition are plotted above, and their corresponding limits and intermediate cases are shown. Adhesion increases the contact area from the Hertz case for a given load by an amount dependent upon the range of attractive forces.\(^6\)
Fig. 4.5 The force-distance for the Dugdale model is shown. A constant stress $\sigma_0$ acts between surfaces over a range $\delta_t$. At greater separation the attractive force is zero.

Dugdale et al., present a self consistent numerical calculation using Lennard-Jones potential with analytical solutions namely Maugis–Dugdale (MD) theory. To approximate an actual interaction potential like that depicted in fig.4.3, Maugis considers a “Dugdale” (square well) potential to describe attractive forces between contacting spheres, fig.4.5, where a constant adhesive stress $\sigma_0$ acts over a range $\delta_t$. Thus the work of adhesion is $\kappa = \sigma_0 \delta_t$. Maugis defines a parameter $\lambda$, which is similar to $\mu$, given by equation 4.5

$$\lambda = 2\sigma_0 \left( \frac{R}{\pi \kappa K^2} \right)^{1/3}$$

(4.5)

where $K$ is the combined elastic modulus of tip and sample, equation 4.6.

$$K = \frac{4}{3} \left( \frac{1 - \nu_1^2}{E_1} \right) + \left( \frac{1 - \nu_2^2}{E_2} \right)^{-1}$$

(4.6)

Here $E_1$ and $E_2$ is the tip and sample Young’s moduli respectively; and $\nu_1$ and $\nu_2$ are the tip and sample Poisson ratios respectively. By choosing $\sigma_0$ to match the minimum adhesive stress of a Lennard–Jones potential, it follows that $\delta_t = 0.97Z_0$, and $\lambda = 1.157\mu$. If $\lambda$ is smaller than 0.1, the solution from MD model is near to that
from the DMT model; and when $\lambda$ is larger than 5, the JKR solution applies. Values between 0.1 and 5 correspond to the transition regime (intermediate) between JKR and DMT cases. Thus, MD model is general solution and can be applied for both the limits and also within the limits which is applied in the current study.

### 4.3 IMPLEMENTING THE THEORIES FOR SOFT MATTER INDENTATION PROBLEM

In recent years, nanoindentation tests are widely used to determine the elastic properties of soft matters (e.g. biomaterials and polymers). For the indentation of soft matter, the effects of adhesion may come into play. In the case that the effect of interfacial adhesion energy is significant, the adhesive contact theories need to be applied to analyze the nanoindentation data \(^{8-11}\). For the adhesive contact of two elastic spheres or a rigid sphere with a flat half-space, we have the JKR \(^{3}\) (Johnson–Kendall–Roberts), DMT \(^{4}\) (Derjaguin–Muller–Toporov) and MD \(^{7}\) (Maugis–Dugdale) theories to use. Greenwood and Johnson \(^{12}\) have developed an adhesion map, which can be applied as a guideline for the selection among these different models. Recently, Yao et al. \(^{13}\) have proposed a corrected adhesion map by taking the strength limit of the materials into consideration. The analytical solutions corresponding to the JKR and DMT theories are simple and easy to use; but these models are only applicable to limited cases. MD model is a general theory; however, the resulting equations are cumbersome and difficult to use in practice as fundamental solutions to extract the material parameters from the indentation response. Carpick et al. \(^{6}\) have proposed a general expression of the correlation between the indentation load and the contact radius; compared with the corresponding relation given by the MD model, which is in much simpler form and easier to apply. Taking into consideration that it is rather difficult or impossible to directly measure the contact radius in nanoindentation tests or the tests based on the atomic force microscope, Pietrement and Troyon \(^{14}\) have presented a generalized equation relating the indentation load to the depth. The generalized equation reported
Chapter 4

INFLUENCE OF SURFACE ENERGY

elsewhere \(^14\) is an exact solution for the DMT and JKR limits, and a very close approximation to the MD theory for the normalized load within the range of -2 to 6 (see [14] for detail). There are also quite a few publications \(^{15-17}\) which use these classic models to analyze the adhesive indentation response. For the methods concerned in this study (e.g. the OP method \(^{18}\) and the methods based on the indentation creep tests), the effects of adhesion are not taken into consideration. These methods have their basis from the hertzian solution where effects of surface forces are not considered. In the present study the MD model (general theory) is used to study a wide range of material from JKR to DMT regime. We will present a solution to simplify the use of the model. The analysis leads to a one-to-one relationship between the indentation response and the transition parameter, which can be determined by using the MD model, fig. 4.6. Therefore, in the use of these methods, one may simply need to know the critical indentation depths beyond which the influence of adhesion can be omitted. In this case, it is useful to propose the results valid for the general adhesive contact problems, from which the common users can easily estimate such critical indentation depths without invoking the adhesive contact theories.

4.3.1 THEORETICAL ANALYSIS

Utilizing the Dugdale model is a reasonable method for the estimating the value of the contact radius and other quantities as a function of load. The indentation load-depth relation from the MD model \(^7\) is determined by the following equations,

\[
\frac{\lambda a_n^2}{2} \left[ \sqrt{m^2 - 1} + (m^2 - 2) \cos^{-1} \left( \frac{1}{m} \right) \right] + \frac{4 \lambda^2 a_n}{3} \left[ \sqrt{m^2 - 1} \cos^{-1} \left( \frac{1}{m} \right) - m + 1 \right] = 1
\]  

(4.7)

\[
P_n = a_n^3 - \lambda a_n^2 \left[ \sqrt{m^2 - 1} + m^2 \cos^{-1} \left( \frac{1}{m} \right) \right]
\]  

(4.8)

\[
\delta_n = a_n^2 - \frac{4 \lambda a_n}{3} \sqrt{m^2 - 1}
\]  

(4.9)
where the parameter \( m \) gives the ratio of the outer radius to the contact radius (see [19] for detail). This set of nonlinear equations 4.7 - 4.9 must be solved in order to fit the contact radius as a function of load. The complete procedure is reported elsewhere\(^6\).

The normalized contact radius, indentation load, and the depth are given by,

\[
\begin{align*}
a_n &= a \left( \frac{4E_r}{3\pi\chi R^2} \right)^{\frac{1}{3}} \\
P_n &= \frac{P}{\pi R \chi} \\
\delta_n &= \delta \left( \frac{16E_r^2}{9\pi^2 R^2 \chi^2} \right)^{\frac{1}{3}}
\end{align*}
\]

where \( a, P, \delta \) are the contact radius, indentation load and the depth, respectively.

Using the MD theory a relationship between indentation load and indentation depth (as recorded by the machine) is established involving the adhesion energy and the transition parameter. Since the OP method used for analyzing the nanoindentation data is based on Hertzian solution. The load-depth behaviour between two solutions (Hertzian, and MD) is studied especially while approaching or retracting from the contact; in order to predict the critical indentation depth beyond which the effects of adhesion can be omitted. In indentation tests, the definition of the initial contact point is important \(^{17, 19-20}\), it should be noted that \( \delta \) in equation (4.12) usually is not the indentation depth recorded in practice. There are a number of different ways to locate the first contact point in nanoindentation\(^9\). In a quasi-static measurement, the initial contact point is usually defined as the point at which the indentation load begins to increase from zero. In this case, the indentation load and the depth recorded by the machine may be given by,

\[
\begin{align*}
P_r &= P \quad (P \geq 0) \\
h &= \delta - \delta_0
\end{align*}
\]
Where $\delta_0$ is the MD contact depth corresponding to $P=0$. When $P_r > 0$, from equation (4.8) we have,

$$m = f_1(\lambda, a_n)$$

(4.14)

From equations (4.8) and (4.9), we obtain

$$P_n = f_2(\lambda, a_n)$$

(4.15)

When $P_r > 0$, there is a one-to-one relationship between $a_n$ and $\delta_n$ for a given $\lambda$; and equations (4.8) and (4.10) give

$$a_n = f_3(\lambda, \delta_n)$$

(4.16)

Inserting equation (4.16) into equation (4.15), we have

$$P_n = f_4(\lambda, \delta_n)$$

(4.17)

The contact radius corresponds to the zero load may be expressed as based on equation (4.15)

$$a_{n,0} = f_5(\lambda)$$

(4.18)

From equations (4.16) and (4.18), we have

$$\delta_{n,0} = f_6(\lambda)$$

(4.19)

Where $\delta_{n,0}$ is the normalized adhesive indentation depth corresponding to $P_n = 0$.

Normalized indentation depth recorded by the machine may be defined as

$$h_n = \delta_n - \delta_{n,0}$$

(4.20)

Equations (4.17), (4.19) and (4.20) give

$$P_n = f_7(\lambda, h_n)$$

(4.21)

From equations (4.11), (4.12) and (4.21), we have
\[ P_n = f_8 \left( \lambda, \frac{h}{z_0} \right) \]  
\[ \text{(4.22)} \]

where \( h \) is the indentation depth recorded by the machine and given by

\[ h = \delta - \delta_0 \]  
\[ \text{(4.23)} \]

From equations (4.12) and (4.22), we have

\[ P_r = \pi R \chi f_8 \left( \lambda, \frac{h}{z_0} \right) \]  
\[ \text{(4.24)} \]

Hertzian solution gives

\[ P_{r,H} = \frac{4}{3} E_r \sqrt{R} h^{3/2} \]  
\[ \text{(4.25)} \]

Diving equation (4.24) with (4.25) gives

\[ \frac{P_r}{P_{r,H}} = \frac{3 \pi \sqrt{R} \chi}{4 E_r h^{3/2}} f_8 \left( \lambda, \frac{h}{z_0} \right) = \frac{3}{4} \pi \left( \frac{\chi^2 R}{E_r z_0^3} \right)^{1/2} \left( \frac{z_0}{h} \right)^{3/2} f_8 \left( \lambda, \frac{h}{z_0} \right) \]  
\[ \text{(4.26)} \]

According to the definition of the Tabor’s parameter, \( \mu \), defined by equation (4.11), and the relation between \( \lambda \) and \( \mu \), equation (4.26) may be rewritten as

\[ \frac{P_r}{P_{r,H}} = f_9 \left( \lambda, \frac{h}{z_0} \right) \]  
\[ \text{(4.27)} \]

\( f_1, f_2, \ldots, f_9 \) in the equations above are functions. Equation (4.27) shows that two dimensionless parameters determine the effects of adhesion. It is noted that equation ...
(4.27) is a general relation which applies to the JKR and DMT models as well. It may even be valid for the cases where the realistic Lennard-Jones potential is applied. By using equation (4.27) and the MD theory, the critical indentation depth has been determined for a wide range of $\lambda$, beyond which the relative difference between $P_r$ and $P_r$, $H$ is smaller than 5%. The results are given in fig. 4.6 when $\lambda$ can be estimated, the critical indentation depth is immediately obtained from the results reported herein; and it is not necessary to invoke the JKR, DMT or MD theories. For instance for the JKR and DMT transition regime ($\lambda$ in the range of 0.1 to 5), the critical indentation depths ($h_c$) predicted by using fig. 4.6 are in range of several to tens nanometers when taking $z_0$=0.4nm.

![Graph showing critical ratios of indentation depth to equilibrium separation](image)

Fig. 4.6 Critical ratios of the indentation depth to the equilibrium separation ($h_c/z_0$) corresponding to different $\lambda$ (beyond the ratios adhesion effects are small)
4.4 EXPERIMENTAL VERIFICATION OF THE THEORETICAL ANALYSIS USING NANOINDENTATION

The surface influence becomes significant at scales where adhesive forces become relevant during contact. The influence of surface energy in the extracted mechanical properties could be studied by considering different polymers like LDPE, PET, PMMA, PP and PS. For the majority of nanomechanical studies on metals, and ceramics surface forces are negligible and the OP method can be directly used to calculate the reduced modulus and hardness values. In the case of surface force dominated interaction the Hertzian analysis will underestimate the contact area and effective load, resulting in an overestimated reduced modulus. Grunlan et al., reported about adhesive forces and their influence over modulus, using an analytical model based on JKR theory for calculating the effective modulus. In the present study, indentations for all the polymers were started from out-of contact point for recording the complete force curve and for calculating the pull-off forces. The indents were initiated from 50nm above the surface so that the process of indentation starts at the same contact condition for all indentation loads. Similar indentation depth ranges were used for testing PMMA, PET, LDPE, PP, and PS. They resulted in a different pull of force responses where the surface energy contributions become relevant, fig. 4.7. A good comparison of the surface energy and pull-off force with the chemical structure is tabulated in table 4.1.

Using the measured pull-off force and the theoretical analysis proposed in previous section we estimate the critical indentation depth, beyond which the effects of adhesion are negligible. In the use of the results given in Fig.4.7, one may simply estimate the parameter $\lambda$ first, and then the critical indentation depth can be easily determined from the figure. We make an attempt to verify the theoretical analysis by experiments. For the tested polymers, we measured the adhesive forces from the force-displacement curves in terms of the pull-off forces ($L_c$). The normalized value of the pull-off force $L_c$ is given by

$$L_c = \frac{L_c}{\pi \lambda R}$$  \hspace{1cm} (4.28)
Using eqs. (11) and (28) we obtain the following relation

$$L_c^*(\lambda) = \frac{1.24L_c}{\pi(E, Z_0^{3/2}, \lambda^{3/2})R^{1/2}} \quad (4.29)$$

The correlation between $\lambda$ and $L_c^*$ is after Carpick et al. $^6$, and given by

$$\Pi_2(\mu) = -\frac{7}{4} + \frac{1}{4} \left( \frac{4.04\lambda^{1.4} - 1}{4.04\lambda^{1.4} + 1} \right) \quad (4.30)$$

An iterative procedure was used to obtain $\lambda$ with a known $L_c$ using equation (4.29) and (4.30). From the obtained $\lambda$ the critical depth is predicted by using fig.4.6. The critical depth at which the surface forces can be neglected is a few to tens of nanometers for all polymers. The theoretical prediction is in good agreement with the experimentally observed values (Fig. 4.8).

![Fig. 4.7 Force – displacement curves for PMMA and PS used for measuring the pull-off force (L_c).](image-url)
Furthermore to understand more about the surface forces the interaction parameter (pull-off force) is studied for different polymers with an indenter. A group of polymer with similar modulus, and surface energy but with different molecular structure was studied with respect to the influence of pull-off forces. For example in PS, PET, and PMMA the difference in the polymer was from phenyl, terephthalate, and acrylate groups in the polymer chain respectively. We may expect from the molecular structural viewpoint, PS and PET with benzene rings to possess a similar pull-off forces. PMMA is the case where surface energy plays a feeble role as observed in fig. 4.7. LDPE with low molecular weight and hydrogen bonding may have the maximum value for the pull-off force. These observations are experimentally supported. The interesting part of this analysis is that the theoretical surface energies for PMMA, PET, and PS are very similar. The reason for having different pull-off force in spite of having similar surface energies clearly explains that the major contributions for the pull-off forces stem from the interacting part of the surface energy, equation (4.31). In our case, the interaction is between the diamond tip and polymer surface. These results are similar to those
reported by Grunlan et al., where they observed strong adhesive forces between polymers and diamond tips, but not for tungsten tip\textsuperscript{21}. Thus, it may be concluded that the above discussions, the interactive part of surface energy is responsible for overestimated reduced modulus. The net surface energy, $\chi$, equation (4.31)

$$\chi = \chi_I + \chi_S - \chi_{I-S} \quad (4.31)$$

where $\chi_I$, $\chi_S$, and $\chi_{I-S}$ are surface energy of the indenter, surface energy of the polymer, and interface energy between the indenter and the polymer, respectively.

<table>
<thead>
<tr>
<th>Polymers</th>
<th>Chemical structure</th>
<th>Pull-off force $L_c$ (µN)</th>
<th>Theoretical surface energy $\gamma_S$ (mJ/Nm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS</td>
<td><img src="image" alt="PS structure" /></td>
<td>1.5</td>
<td>43.0</td>
</tr>
<tr>
<td>PMMA</td>
<td><img src="image" alt="PMMA structure" /></td>
<td>0.15</td>
<td>39.0</td>
</tr>
<tr>
<td>PET</td>
<td><img src="image" alt="PET structure" /></td>
<td>1.4</td>
<td>41.3</td>
</tr>
<tr>
<td>PP</td>
<td><img src="image" alt="PP structure" /></td>
<td>0.8</td>
<td>31.0</td>
</tr>
<tr>
<td>LDPE</td>
<td><img src="image" alt="LDPE structure" /></td>
<td>1.8</td>
<td>31.0</td>
</tr>
</tbody>
</table>

Table.4.1 Investigated polymers with chemical structure, theoretical surface energy, and measured pull-off forces in this work (5µm spherical indenter)
4.5 CONCLUSIONS

We showed in this study that two dimensionless parameters, i.e. the ratio of the indentation depth to the equilibrium separation \( \frac{h}{z_0} \) and the parameter \( \lambda \) determine the adhesion effects by using the MD theory. This is a general solution which applies to the JKR, DMT and MD models. In the OP method and also the method based on the indentation creep tests, adhesion effects are not considered. When using the OP method or for indentation creep tests, the maximum indentation depth should be larger than \( h_c \) in order to avoid the adhesion effects in retrieving the mechanical properties.

Using experiments we have identified the critical indentation depth for various polymers using the measured pull-off force. The experiments and theoretical predictions are in good agreement with each other. Furthermore, it is understood from our study that the measured pull-off force is the interactive part of surface energy (interaction between the indenter and the polymer).

REFERENCES


CHAPTER 5

5. IDENTIFYING THE LIMITATION OF OLIVER AND PHARR METHOD WITH RESPECT TO INDENTER GEOMETRY

5.1. INTRODUCTION

Nanoindentation tests are widely used in recent years to characterize the mechanical properties of viscoelastic-plastic materials like polymers, biomaterials at the micro or nano-scales. In most cases, the procedure proposed by Oliver and Pharr (OP method) by improving the method of Doerner and Nix is adopted. However, recent studies revealed that the mechanical properties of viscoelastic-plastic materials determined using the OP method leads to the incorrect evaluation of the reduced modulus. Usually pile-up, viscoelasticity, or adhesion energy is considered as the most important reasons for the failure of the OP method. The purpose of this thesis is to systematically study the actual limitations of the OP method; from chapter 2 to chapter 4 theoretical and experimental study of the above mentioned issue are examined. By computational and experimental study it is understood from previous chapters an experimental procedure can avoid viscoelastic effects in modulus determination. Pile up does not play a major role on determining the analysis of the force curves at relatively smaller depths. In chapter 4 it is identified that adhesion energy play an important role in overestimating the contact area for depths less than a critical depth beyond which the influence of adhesion energy is negligible. All the results reported are for spherical indenter and suggest that pile-up, viscoelasticity, or the effect of surface forces (adhesion energy) could be avoided while determining the reduced modulus. We made efforts to extend our experience in spherical indenter to Berkovich indenter for same polymers which failed to obtain the correct reduced modulus. Thus the motivation of this chapter is to understand the possible factors for the failure of the OP method for Berkovich indenter. A novel work
performed by Tranchida et al.,\textsuperscript{11} provides the bottle neck information for the failure of OP method on polymers. They argue that OP procedure or any other procedure derived from elastic contact mechanics cannot be applied to viscoelastic materials even with the designed experimental procedure. This is in contradiction to the results obtained for viscoelastic materials using spherical indenter in our case. According to Tranchida et al.,\textsuperscript{11} the failure of the OP method is from the hypothetical area function used from the polymer. The area function representing the indenter geometry is different for different polymers, implying that every polymer shows its own unique contact behavior\textsuperscript{13}. According to these reports a universal calibration material does not exist for viscoelastic-plastic materials (polymers). In most cases, quartz or fused silica is used as the standard calibration material, and the calibration procedure proposed by Oliver and Pharr (OP) is widely applied. However, for indenting softmatter (polymer and biological materials) the use of calibration material and procedure is not explicit. Moreover, using a calibration material (polymer, quartz or soft metal) to evaluate the mechanical properties for viscoelastic-plastic materials through the OP method will always cause uncertainties.

In this chapter a systematic experimental study is performed with different materials using different indenters like spherical and Berkovich geometries. Nanoindentation experiments were performed on different kinds of materials viz: quartz, soft metal (antimony, and platinum), and polymers (low-density polyethylene, polystyrene, polyethylene terephthalate, polymethyl methacrylate, and polypropylene). Area function obtained for all the materials using both the indenters are compared to the tip shape function extracted from scanning electron microscope images. This systematic study of choosing a calibration material and the calibrating method with respect to different indenter geometries for measuring polymers can elucidate the artifacts from the geometry. Results from this study can help us understand the reasons for the failure of OP method for viscoelastic-plastic materials. These findings will have significant practical implications for the analysis of nanoindentation load versus indenter displacement data for viscoelastic-plastic materials obtained from different indenters.
CHAPTER 5  IDENTIFYING THE LIMITATION OF OLIVER AND PHARR METHOD WITH RESPECT TO INDETER GEOMETRY

5.2. EXPERIMENTS

5.2.1. MATERIALS

In order to identify an appropriate calibration material for measuring polymers we choose material of three different kinds with varying hardness or modulus from low to high values. Quartz (standard calibrating material), soft metal (moderate hardness), and polymers (lower hardness) are chosen. Usually Al (aluminum) with moderate hardness is used in literature as a calibrating standard, but for low penetration depths the oxide layer challenges the homogeneity of the calibrating material across the depth. Therefore, Sb (antimony) and Pt (platinum) were chosen for its homogenous surface property. To provide a broad property selection for viscoelastic-plastic materials, polymers exhibiting different mechanical properties are studied ranging from amorphous to semi-crystalline structure and from glassy to rubbery mechanical behavior. The investigated polymers are: low-density polyethylene (LDPE), polystyrene (PS), polyethylene terephthalate (PET), polymethylmethaacrylate (PMMA) and polypropylene (PP) (GoodFellow). The mechanical homogeneity of all the materials was verified by microindentation (Fischerscope) refer appendix. Local surface roughness for all samples was measured by atomic force microscopy (AFM) (Veeco Metrology Group, Dimension TM 3100) and was a negligible value (< 5nm) for all materials, fig.5.1 but quartz (14nm).

5.2.2 NANOINDENTATION

Nanomechanical characterization was performed for all chosen materials with a Hysitron Triboscope (Hysitron Inc.), for more information refer chapter 3. A spherical and a Berkovich indenter with a 5μm and 200nm tip radius respectively are applied in displacement controlled mode. Field Emission Scanning Electron Microscope (FE-SEM, LEO 1550VP, GEMINI) images were made to observe the actual dimensions of the tip. These images were used to map the tip radius, and face angle for spherical and Berkovich indenters and was estimated as ~5.3μm and ~60° respectively. The area function describing the real indenter profile used for indentation experiments requires a precise calibration, especially when taking tip imperfections or
irregularities into consideration. The calibration procedure is briefly discussed here. The procedure requires using a standard material with uniform and well-known material properties (especially the Young’s modulus, eg. quartz) for determining the area function. The area function is obtained for all the materials using the same procedure for a contact depth ranging from 5nm to 300nm for both the indenters. The calibration procedure was repeated several times and no significant change in the area function was observed. Each indent was made using a trapezoidal loading function in which the indentation depth was first increased to the maximum set value and then held at the peak value before fast unloading (this procedure avoids viscoelastic effects for polymers), fig.5.2. In each case, an array of ten indents at five different places was made for all chosen materials. The maximum thermal drift was 0.027nm/s before starting the indentation and drift correction was used to minimize thermal effects. All the experiments were performed at room temperature.

Fig.5.1 AFM surface profile with scan size 10µm x 10µm polystyrene (PS) depicting the surface roughness.
5.2.3. OLIVER & PHARR METHOD

In depth-sensing instrumented indentation (nanoindentation) tests, the material properties are extracted from the force-depth curve. The OP formulation yields

$$E_r = \frac{\sqrt{\pi} S}{2\gamma \sqrt{A_c}}$$  \hspace{1cm} (5.1)$$

where,

$$S = \frac{dP}{dh} \bigg|_{(P_m, h_m)}$$ \hspace{1cm} (5.2)$$

$$A = f(h_c)$$ \hspace{1cm} (5.3)$$

The contact stiffness ($S$) is determined from the initial unloading slope evaluated at maximum indentation depth ($h_m$) or maximum indentation load ($P_m$) as in eqn. (5.2). The
contact area ($A_c$) is related to the contact depth ($h_c$) by the area function eqn. (5.3), which can be determined experimentally through the calibration procedure discussed above. The reduced modulus $E_r$ is calculated from the measured $S$, and $A_c$ to correct the effects from indenter geometry, using equation (5.1).

5.3. RESULTS AND DISCUSSIONS

5.3.1 COMPARING AREA FUNCTION FROM SPHERICAL AND BERKOVICH INDENTER

It is known from previous reports the uncertainties in OP method in measuring the actual properties is from the area function for viscoelastic-plastic materials, and the aim of this study is to address this issue with respect to different indenter geometries. A method to perform calibration or the use of calibration material requires serious attention in the growing softmatter nanoindentation community. We address this problem by using materials of different kinds in order to suggest a calibration material and a procedure for polymers. Generally a standard calibration material (quartz or fused silica) is used or a tip shape function is directly extracted from an AFM or SEM images\textsuperscript{14-15} to calibrate the tip. Researchers suggest in directly using the tip shape function which can avoid error due to serious tip defects from the indenter geometry. For characterizing polymers a standard calibrating material or method is subjected to controversy though polycarbonate is often used in literature as a calibration material. Indentations were performed on all chosen materials and the area functions for both the indenters are extracted using the same experimental protocol, fig.5.2. The area function is obtained from three different kinds of materials viz: quartz, polymer, and soft metals are compared to the tip shape function of the indenter. We calculated the tip shape function for both indenters, based on the tip angle and tip radius extracted from SEM images, which
provides the limit for all the tested materials, eqn. (5.4).

\[ A = \pi a^2 = -\pi h_c^2 + -2\pi Rh_c \]  

spherical geometry (5.4a)

The theoretical formula used for plotting the area function for spherical indenter is given in eqn. (5.4a) and 5.3μm is used as radius of the indenter (R) from SEM, fig. 5.3a.

![5.3μm spherical indenter](image)

Fig. 5.3a Scanning electron microscopy image of the spherical indenter with the mapped tip radius.

\[ A = 24.5h_c^2 + C_1h_c + C_2h_c^{1/2} + C_3h_c^{1/4} + C_4h_c^{1/8} + \ldots \]  

Berkovich geometry (5.4b)

where are constants determined by curve fitting. For Berkovich indenter is 24.5, but is modified as 27.8 based on the face angle value from SEM, fig. 5.3b (60° instead of 65°.35), and is used as the tip shape function.
The contact depth and contact area relation for all the tested materials with the tip shape function for both spherical and Berkovich indenter are plotted respectively in fig. 5.4a, and 5.4b. The following are the very first observation that is noticed in these plots. 1) It is apparent from the plots that the mechanical or the contact behavior of polymers is very much dependent on the indenter geometry. 2) The area function for polymers is very much different in fact several orders higher than the standard calibrating material, and soft metal. This observation is noticed independent of indenter geometry i.e., for both spherical and Berkovich indenters. 3) It is clear from these plots that the standard calibrating material or soft metal, or the tip shape function (from AFM or SEM) cannot be used for calibrating polymers. Thus, only a polymer can be used as a calibrating material for characterizing the nanomechanical properties of polymer with the current OP method. The next logical question to be answered is can any polymer be used as a calibration material for measuring viscoelastic-plastic materials (polymers). To solve this issue
we studied different polymers with varying microstructure and mechanical properties. The area function is obtained for all polymers using both the indenter to avoid artifacts from indenter geometry and to address the scientific uncertainties reported by previous researcher’s \textsuperscript{11, 13}. Fig. 5.5a, 5.5b shows the area function plots for the spherical and Berkovich indenters for a variety of polymers. The results from the spherical indenter, fig.5.5a suggest that any homogenous polymer with well known modulus values can be used as a calibrating material for characterizing soft matter (viscoelastic-plastic materials). A designed experimental protocol with the existing OP method can minimize viscoelasticity in obtaining the correct mechanical properties and the effects like pile-up and adhesion can be avoided by considering the critical indentation depth \textsuperscript{16} for spherical indentation. But the results from the Berkovich indenter were not in congruence with the spherical indenter. It is evident from fig.5.5b the contact depth vs the contact area relation obtained for Berkovich indenter were different for different polymers similar to reported elsewhere \textsuperscript{11, 13}. To the best knowledge of authors we are the first to observe this prominent difference in the obtained area function between different indenter geometries. We propose few possible reasons for this tremendous difference in material behavior between different indenters. It could be due to the geometry of the indenter (inappropriate definition of the geometry), the complexity arising from the material mechanics or, the molecular length scales influencing the results. Considering the above issues the discussions and analysis of the obtained results are performed for spherical and Berkovich geometries. The primitive and the imperative issue to be clarified in terms of indenter geometry are the tip defects. The contact depth vs contact area relation for quartz and soft metal is similar to tip shape function (from SEM) for Berkovich geometry, fig.5.5b. This information confirms that for Berkovich geometry, tip defect is not responsible for the variation observed between polymers in the area function. Another important factor concerning the geometry is the OP analysis itself based on Doerner and Nix\textsuperscript{4} initially applied to cylindrical punch case to determine the properties. The analysis is based on axisymmetric geometry or a rigid body revolution in an elastic-half space. It is well applicable for spherical indenter, but Berkovich is considered as a cone with half angle of 70.30 which a crude approximation\textsuperscript{13}. 
Furthermore, from the work of Lim et al.\textsuperscript{13}, they concluded that approximating a pyramidal indenter (Vickers geometry) as a cone is not valid. They performed in-situ measurements and studied the projected contact area, which was significantly different from the theoretically predicted equivalent rigid cone with semi-included angle of 70.30. This report is similar to our case which further confirms that the approximation of Berkovich geometry to cone must be crucially examined. All analyses to date have ignored the fact that there are sharp edges on the indenter. These undoubtedly influence the nature of the stress fields, even at the shallowest depths, as evidenced by the observation that images even the smallest impression are usually triangular in appearance rather than circular\textsuperscript{17}. The above results and the discussions in this section make us comment that the theoretical basics for the OP analysis method for measuring viscoelastic-plastic materials are strongly dependent on the indenter geometry.

![Graph](image)

Fig. 5.4a A contact depth – contact area plot for spherical indenter obtained for different materials is shown.
Fig. 5.4b A contact depth – contact area plot for Berkovich indenter for different kinds materials is shown.

Fig. 5.5a Contact depth – contact area plot for spherical indenter (5µm) for different polymers is plotted.
Another important factor that is responsible for this variation between indenter geometries can be from viscoelastic-plastic material mechanics. Indeed we also make an attempt to discuss the possible causes for the difference in the area function response between indenters, and between polymers for Berkovich geometry. From the material mechanics view point the difference between the two indenters arises from strain, strain gradients, hydrostatic pressure beneath the indented surface which may influences the state of the polymer (glass transition temperature). In either case, the probed material could restrict molecular mobility in the confined region of mechanical contact adjacent to the probe, either via intermolecular interaction (enthalphic) or via stretching on alignment of macromolecular chains with respect to the probe surface (entropic via reduced conformations – strain hardening), refer chapter 3. The non-linear nature of the yield process and the strain softening character of polymer results in localization of deformation as plastic strain increases. The extent to which polymer are susceptible to strain localization is determined by a subtle interplay between strain...
softening which allows the zone to grow with decreasing stress, and the amount of strain hardening determines the stability of the deformation zone. The relative volumetric proportion of strained polymer beneath the probe is smaller for Berkovich leading to high or severe localization when compared to 5μm spherical indenter. Here we estimate the extent of localization by considering the molecular weight, Rg (radius of gyration) which represents the molecular length and comparing to the dimensions of the indenters. This comparison can explain the length scales at which the properties of the polymer are actually probed. Rg calculated for all the polymers where between 20 to 200nm. Thus the ratio of Rg to indenter radius for spherical indenter (5μm) and Berkovich indenter (200nm) varies from 0.4% to 4% and from 10% to 100% respectively for all polymers. This analogy can help us understand the severe localization occurring in molecular level for Berkovich geometry. It can be that, the strain softening and strain hardening (post-yielding behavior) is captured by Berkovich indenter but not by spherical indenter. In the case of severe localization occurring under Berkovich indenter for polymer the extracted data will depend on the molecular weight, processing temperature, tacticity, crystalinity, etc., and all of these parameters can play a vital role in retrieving properties. This can be responsible for the prominent differences in area function observed between the two geometries. If this is the case then the tip shape function for sharp indenters will depend on the molecular structure or microstructure and will be different for every polymer, and a unique area function will be obtained for every tested polymer. Thereby, measuring the material properties may not be possible. Small spherical indenter to the extent they can be obtained and calibrated would avoid the edge problem and the localization in the determining the properties of soft matter.

5.4 CONCLUSIONS

The following are some of the important conclusions that are drawn from this work. The mechanical or the contact behavior of polymers is very much dependent on the indenter geometry. From our study we identified that using a designed protocol and at shallow
indentation depth it is feasible to use spherical indenter in obtaining the macroscopic properties of polymers, but not with Berkovich geometry. The Berkovich geometry theoretically approximated as a cone with strong edges causes severe localization in the material. This resulted in the unique contact law behavior for every tested polymer. It is concluded that the OP method in conjunction with Berkovich geometry cannot be used to measure the mechanical properties of viscoelastic-plastic solids (polymers). Moreover for measuring polymers irrespective of the indenter geometry a homogenous polymer has to be used as a calibrating material. Area function from SEM or AFM which gives the actual tip profile will leads to overestimation in the obtained properties. A small spherical indenter can avoid the edge problem, and the localization in the determining the properties of soft matter. A spherical indenter in conjunction with the experimentally designed protocol, and a standard polymer as a calibrating material can be used to retrieve reliable properties of viscoelastic-plastic solids.

REFERENCES


16. B Keerthika, Y P Cao, D Raabe: Mechanical characterization of viscoelastic-plastic soft matter using spherical indentation (in review)


CHAPTER 6

6. CONCLUSIONS AND OUTLOOK

Nanoindentation tests are widely used in recent years to characterize the nanomechanical properties of viscoelastic-plastic materials (polymer), the analysis method proposed by Oliver & Pharr (OP) is widely adopted. However, recent studies revealed that the mechanical properties of viscoelastic-plastic materials determined using the OP method might exhibit significant errors, which are as follows. The presence of viscoelastic deformation can underestimate the reduced modulus, or due to the plastic deformation the indented material might exhibit piling-up, and overestimate the reduced modulus. Moreover, adhesion energy between the contact surfaces may play an important role in characterizing polymers. Based on the issues above, we further examine the applicability of the OP method for characterizing the nanomechanical properties of viscoelastic-plastic materials, placing special emphasis on the reduced (instantaneous) modulus. A number of fundamental issues regarding the spherical indentation of viscoelastic-plastic soft matter are examined via finite element analysis based on a viscoelastic plastic model and the adhesive contact theories. In summary, the following contributions have been made.

In chapter 2, the fundamental relations used in the OP method are examined by using finite element analysis based on a viscoelastic plastic model. The analysis shows that the correlation between the initial unloading slope, reduced modulus and the projected contact area may hold true even the indented material undergoes viscoelastic and plastic deformation simultaneously. This is when sufficiently fast loading, holding at maximum displacement, and fast unloading can be used as a experimental protocol. Effects of the time-dependent deformation behavior and the plastic deformation on the determination of the contact area is studied in chapter 2. The computational results also show that the realtion may be applicable if in which the maximum indentation load corresponding to a fast loading rate and at the beginning point of the holding segment is used for a displacement-controlled indentation. The analysis eventually leads to a loading-holding-unloading protocol, following which and use the
standard OP method, instantaneous modulus may be reliably determined. Experiments are performed on four kinds of polymers i.e., PET, LDPE, PP, and PS, to validate the protocol identified from numerical analysis and the results. The procedure is successfully used independent of the nature of soft matter (viscoelastic-plastic material) and is consistent in different deformation regimes as discussed in chapter 3.

Considering the limitations in the OP method, a number of novel techniques have been proposed in recent years to determine the mechanical properties of time-dependent materials. We discussed in chapter 2 the effects of plastic deformation on the methods based on indentation creep tests in determining the viscoelastic properties of polymers. We highlight the effects of the plastic deformation by using finite element simulations based on the viscoelastic-plastic model. In the sequel, we determined the critical ratios of $h_{\text{max}}/R$ (indentation depth /tip radius)beyond which the effects of plastic deformation are significant. By using the results proposed herein and some prior knowledge about the ratio of $\sigma_y/E_p$, (initial yield stress/ elastic moduli of the elastoplastic network) one can estimate the proper ratios of $h_{\text{max}}$ to $R$ to ease the effects of plastic deformation when setting up the experiments.

Adhesion effects are addressed. In the OP method and also the method based on the indentation creep tests, adhesion effects are not considered. Thus the users of these methods need to know the critical indentation depth beyond which the effects of adhesion are negligible. We showed in chapter 4 that two dimensionless parameters, i.e. the ratio of the indentation depth to the equilibrium separation ($h/z_o$) and the parameter $\lambda$ determine the adhesion effects. This is a general solution which applies to the JKR, DMT and MD models. We determined the critical ratios of the indentation depth to the equilibrium separation ($h_c/z_o$) by using the MD theory for a wide range of $\lambda$ (from 0.01 to 100). Using the results reported herein, the critical indentation depth $h_c$ can be evaluated without invoking different adhesive contact theories. Using experiments we have identified the critical indentation depth for various polymers using the measured pull-off force. The experiments and theoretical predictions are in good agreement with each other (chapter 4). Furthermore, it is understood from our study that
the measured pull-off force is the interactive part of surface energy (interaction between the indenter and the polymer).

From our study we identified that a spherical indenter in conjunction with the experimentally designed protocol, and a standard polymer as a calibrating material can be used to retrieve reliable properties of viscoelastic-plastic solids. Indeed, being aware of the critical indentation depth and the maximum indentation depth at which the creep test stops (creep tests). We made efforts to extend this protocol to pyramidal indenter (berkovich geometry) but was not successful. The berkovich geometry theoretically approximated as a cone with strong edges causes severe localization in the material. This resulted in the unique contact law behaviour for every tested polymer. The mechanical or the contact behaviour of polymers is very much dependent on the indenter geometry (chapter 5).

It is finally concluded from our research that the OP method in conjunction with the developed experimental protocol using a spherical indenter can avoid the edge problem, and the localization in the determining the properties of soft matter. The problem of polymer mechanics showing different response for various indenters requires serious attention in the rapidly growing soft matter nanoindentation community, where most of the experiments are performed using berkovich indenter being unaware of the existing uncertainties.
CHAPTER 7

APPENDICES

APPENDIX A: ADDITIONAL INFORMATION TO CHAPTER 3

The materials low density polyethylene (LDPE), polystyrene (PS), polyethylene terephthalate (PET), and polypropylene (PP) were selected and studied in chapter 3, because their mechanical properties are well known and thus offer a good possibility to compare our results to results from completely independent measurements. In the following, the material properties specified by the manufacturers are summarized.

**Polystyrene:**

<table>
<thead>
<tr>
<th>Mechanical Properties</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Elongation at break ( % )</td>
<td>1.6</td>
</tr>
<tr>
<td>Hardness - Rockwell</td>
<td>M60-90</td>
</tr>
<tr>
<td>Izod impact strength ( J m⁻¹ )</td>
<td>19-24</td>
</tr>
<tr>
<td>Poisson's ratio</td>
<td>0.35</td>
</tr>
<tr>
<td>Tensile modulus ( GPa )</td>
<td>2.3-4.1</td>
</tr>
<tr>
<td>Tensile strength ( MPa )</td>
<td>30-100</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Physical Properties</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Abbe number</td>
<td>30.8</td>
</tr>
<tr>
<td>Density ( g cm⁻³ )</td>
<td>1.05</td>
</tr>
<tr>
<td>Limiting oxygen index ( % )</td>
<td>19</td>
</tr>
<tr>
<td>Refractive index</td>
<td>1.59-1.60</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Thermal Properties</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coefficient of thermal expansion ( x10⁻⁶ K⁻¹ )</td>
<td>30-210</td>
</tr>
<tr>
<td>Heat-deflection temperature - 0.45MPa ( C )</td>
<td>90</td>
</tr>
<tr>
<td>Heat-deflection temperature - 1.8MPa ( C )</td>
<td>80</td>
</tr>
<tr>
<td>Specific heat ( J K⁻¹ kg⁻¹ )</td>
<td>1200</td>
</tr>
<tr>
<td>Thermal conductivity @23C ( W m⁻¹ K⁻¹ )</td>
<td>0.1-0.13</td>
</tr>
<tr>
<td>Upper working temperature ( C )</td>
<td>50-95</td>
</tr>
</tbody>
</table>
**Polymethyl methacrylate:**

**Mechanical Properties**
- Elongation at break ( % ) 2.5-4
- Hardness - Rockwell M92-100
- Izod impact strength ( J m$^{-1}$ ) 16-32
- Poisson's ratio 0.35 - 0.4
- Tensile modulus ( GPa ) 2.4-3.3
- Tensile strength ( MPa ) 80

**Physical Properties**
- Abbe number 57.2
- Density ( g cm$^{-3}$ ) 1.19
- Flammability HB
- Limiting oxygen index ( % ) 17-20
- Radiation resistance Fair
- Refractive index 1.49
- Resistance to Ultra-violet Good
- Water absorption - over 24 hours ( % ) 0.2

**Thermal Properties**
- Coefficient of thermal expansion ( x10$^{-6}$ K$^{-1}$ ) 70-77
- Heat-deflection temperature - 0.45MPa ( C ) 105
- Heat-deflection temperature - 1.8MPa ( C ) 95
- Lower working temperature ( C ) -40
- Specific heat ( J K$^{-1}$ kg$^{-1}$ ) 1400 - 1500
- Thermal conductivity @23C ( W m$^{-1}$ K$^{-1}$ ) 0.17-0.19
- Upper working temperature ( C ) 50 to 90

**Polypropylene:**

**Mechanical Properties**
- Abrasive resistance - ASTM D1044 ( mg/1000 cycles ) 13-16
- Coefficient of friction 0.1-0.3
- Elongation at break ( % ) 150-300
- Hardness - Rockwell R80-100
- Izod impact strength ( J m$^{-1}$ ) 20-100
- Tensile modulus ( GPa ) 0.9-1.5
- Tensile strength ( MPa ) 25-40
### Physical Properties

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (g cm(^{-3}))</td>
<td>0.9</td>
</tr>
<tr>
<td>Flammability</td>
<td>HB</td>
</tr>
<tr>
<td>Limiting oxygen index (%)</td>
<td>18</td>
</tr>
<tr>
<td>Refractive index</td>
<td>1.49</td>
</tr>
<tr>
<td>Water absorption - equilibrium (%)</td>
<td>0.03</td>
</tr>
</tbody>
</table>

### Thermal Properties

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coefficient of thermal expansion (\times 10^{-6} \text{ K}^{-1})</td>
<td>100-180</td>
</tr>
<tr>
<td>Heat-deflection temperature - 0.45MPa (C)</td>
<td>100-105</td>
</tr>
<tr>
<td>Heat-deflection temperature - 1.8MPa (C)</td>
<td>60-65</td>
</tr>
<tr>
<td>Lower working temperature (C)</td>
<td>-10 to -60</td>
</tr>
<tr>
<td>Specific heat (\text{J K}^{-1} \text{kg}^{-1})</td>
<td>1700 - 1900</td>
</tr>
<tr>
<td>Thermal conductivity @23C (\text{W m}^{-1} \text{K}^{-1})</td>
<td>0.1-0.22</td>
</tr>
<tr>
<td>Upper working temperature (C)</td>
<td>90-120</td>
</tr>
</tbody>
</table>

### Polyethylene terephthalate:

#### Mechanical Properties

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coefficient of friction</td>
<td>0.2-0.4</td>
</tr>
<tr>
<td>Hardness - Rockwell</td>
<td>M94-101</td>
</tr>
<tr>
<td>Izod impact strength (\text{J m}^{-1})</td>
<td>13-35</td>
</tr>
<tr>
<td>Poisson's ratio</td>
<td>0.37-0.44</td>
</tr>
<tr>
<td>Tensile modulus (\text{GPa})</td>
<td>2-4</td>
</tr>
<tr>
<td>Tensile strength (\text{MPa})</td>
<td>80</td>
</tr>
</tbody>
</table>

#### Physical Properties

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (g cm(^{-3}))</td>
<td>1.3-1.4</td>
</tr>
<tr>
<td>Flammability</td>
<td>HB</td>
</tr>
<tr>
<td>Limiting oxygen index (%)</td>
<td>21</td>
</tr>
<tr>
<td>Refractive index</td>
<td>1.58-1.64</td>
</tr>
<tr>
<td>Water absorption - equilibrium (%)</td>
<td>&lt;0.7</td>
</tr>
<tr>
<td>Water absorption - over 24 hours (%)</td>
<td>0.1</td>
</tr>
</tbody>
</table>
Low density polyethylene:

**Mechanical Properties**

- Elongation at break ( % ) 400
- Hardness - Rockwell D41-46 - Shore
- Izod impact strength ( J m⁻¹ ) >1000
- Tensile modulus ( GPa ) 0.1-0.3
- Tensile strength ( MPa ) 5-25

**Physical Properties**

- Density ( g cm⁻³ ) 0.92
- Flammability HB
- Limiting oxygen index ( % ) 17
- Refractive index 1.51
- Water absorption - over 24 hours ( % ) <0.015

**Thermal Properties**

- Coefficient of thermal expansion ( x10⁻⁶ K⁻¹ ) 20-80
- Heat-deflection temperature - 0.45MPa ( C ) 115
- Heat-deflection temperature - 1.8MPa ( C ) 80
- Lower working temperature ( C ) -40 to -60
- Specific heat ( J K⁻¹ kg⁻¹ ) 1200 - 1350
- Thermal conductivity @23C ( W m⁻¹ K⁻¹ ) 0.15-0.4
- Upper working temperature ( C ) 115-170
APPENDIX A: ADDITIONAL INFORMATION TO CHAPTER 3 AND 5

Microindentation tests were performed for all the materials to test the mechanical homogeneity and in obtaining a reference modulus value for all material apart from manufactures value. The microindenter from Fischerscope is operated with the Vickers indenter. Microhardness is the hardness of a material as determined by forcing an indenter such as a Vickers, Brinell, or Knoop indenter into the surface of the material under load; usually, the indentations are measured with a microscope. It is the standard method for measuring the hardness of metals, particularly those with extremely hard surfaces: the surface is subjected to a standard pressure for a standard length of time by means of a pyramid-shaped diamond. The indenter employed in the Vickers test is a square-based pyramid whose opposite sides meet at the apex at an angle of 136°. From the residual impression left over the opposite diagonals are measured under microscope to obtain Vickers number (HV) using the formulae given below in equations (7.1)

\[
HV = \frac{2F \sin 136/2}{d^2}
\]  

(7.1)

where, F being the applied load (measured in kilograms-force) and \(d^2\) the area of the indentation (measured in square millimetres). The obtained reduced modulus for different material is tabulated in the table.7.1. The maximum indentation load of 20 mN with a loading rate of 20 mNs\(^{-1}\) is used for all materials.

<table>
<thead>
<tr>
<th>Material</th>
<th>Reduced modulus (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polymethyl methacrylate</td>
<td>4.90</td>
</tr>
<tr>
<td>Low density polyethylene</td>
<td>0.31</td>
</tr>
<tr>
<td>Polyethylene terephthalate</td>
<td>3.55</td>
</tr>
<tr>
<td>Polypropylene</td>
<td>1.34</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>3.90</td>
</tr>
<tr>
<td>Antimony</td>
<td>26.06</td>
</tr>
<tr>
<td>Platinum</td>
<td>79.00</td>
</tr>
</tbody>
</table>

Table.7.1. Reduced modulus for different material measured using microindentation.
Papers and Proceedings:

1. Identifying the limitation of Oliver and Pharr method in characterizing the viscoelastic-plastic materials with respect to indenter geometry; Keerthika Balasundaram, Yanping Cao, Dierk Raabe; Nano- and Microscale Materials—Mechanical Properties and Behavior under Extreme Environments, MRS Proceedings, 1137-EE10-23.

2. Mechanical characterization of viscoelastic-plastic soft matter using nanoindentation; Keerthika Balasundaram, Yanping Cao, Dierk Raabe (in review)

Presentations (Talks and Posters):


2. Investigating the Applicability of the Oliver & Pharr Method to the Nano-Mechanical Characterization of Soft Matter; Keerthika Balasundaram, Yanping Cao, Dierk Raabe; Gerberich Symposium, 1st International Conference from Nanoparticles and Nanomaterials to Nanodevices and Nanosystems, Halkidiki, Greece, 16-18 June, 2008. (Talk)

3. Identifying the limitation of Oliver and Pharr method in characterizing the viscoelastic-plastic materials with respect to indenter geometry; K. Balasundaram, Y.P Cao, D. Raabe; 2008 MRS Fall Meeting, December 1 - 5, Boston, MA, U.S.A (Poster)
Name: Keerthika Balasundaram

Date and Place of Birth: 16.01.1983, Coimbatore (Tamilnadu, India)

Nationality: Indian

Education:

- Since 13.02.2006 IMPRS-SurMat Scholar - Department of Microstructure Physics and Metal Forming, (Head: Prof.Dr.D.Raabe ), Max-Planck-Institut für Eisenforschung GmbH, Düsseldorf, Germany. Registered as a Ph.D Student at Fakultät für Maschinenbau (Prof. Dr.-Ing. G. Eggeler), Ruhr-Universität, Bochum, Germany.

- 2005 M.Sc (Materials Science) - P.S.G College of Technology (affiliated to Anna University), Coimbatore, India. Thesis title: Noble metal coatings on titanium for nuclear fuel reprocessing plant applications

- 2003 B.Sc (Applied Science) - P.S.G College of Technology (affiliated to Bharathiar University), Coimbatore, India.
