Interaction between Polystyrene Spheres by Atomic Force Microscopy

By

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ABSTRACT

The interaction between a single polystyrene particle and a polystyrene substrate has been previously reported by a number of investigators. However, the effects of relative humidity, applied load and contact time on the adhesion of polystyrene surfaces have not been investigated and these effects are poorly understood. It is the primary aim of the current work to characterise the effect of the aforementioned parameters on the adhesion of polystyrene surfaces using atomic force microscopy. The polystyrene used in this study contained 1% of di-vinyl benzene as a cross-linking agent.

The adhesion forces between an individual polystyrene particle, normally 12-14 μm in diameter, and the surface of a compacted tablet of the same material have been measured at various relative humidities using a custom-built instrument and a commercial AFM. The commercial instrument has the capability of scanning the sample surface, and allowing greater control over the relative motion between the sample and probe. One of the achievements of this work is that a technique has been developed whereby an image of the surface of the tablet can be obtained using the attached particle as a probe scanning in non-contact mode.

From the work conducted using the custom-built instrument, the dependency of adhesion forces on the relative humidity is greatest at relative humidities above 60% where capillary forces cause a sharp increase in adhesion with increasing relative humidity. Hysteresis was observed in the solid-solid contact gradient of the accompanying force curves, suggesting non-elastic behaviour at the contact area of the surfaces. Using the commercial AFM it was observed that adhesional values are consistently higher than results obtained from the custom built instrument across the range of relative humidities from 2% RH to 50% RH. This is due to the selection of smooth, single particle contact sites in the commercial AFM experiments.

The measured adhesional forces from the custom-built instrument were found to be significantly lower than predictions for adhesion from the contact mechanics theories of JKR and DMT. This can be attributed to the effect of surface roughness and multiple contacts, which are not taken into account in either the JKR or DMT contact mechanics theories. At humidities below 60%
the results obtained from the commercial AFM are in much better agreement with the predicted pull-off forces from the JKR model, because smooth, single particle contact regions could be selected.

Using the custom-built instrument and the AFM Explorer, the effect of applied load on the adhesion force between a polystyrene particle and a polystyrene substrate was studied at low, medium and high relative humidities. Increasing the applied load has little effect on the measured adhesion forces at low and medium relative humidities but at high relative humidities of 60 to 65% RH, a transition was observed at an applied load of 1000 – 1200 nN. Above this transition the adhesion force increased steadily with applied load due to the yield stress of the material in the contact region being exceeded.

The experimental values of applied load have been coupled with published values of Young’s modulus, Poisson’s ratio and hardness to predict the contact area from contact mechanics models of JKR and Maugis-Pollock. When coupled with the published value of yield stress for the material, the applied load for the onset of plastic flow is predicted. The value of 1508 nN predicted by the plasticity-based MP model agrees approximately with the observed transition in behaviour.

A study on the effect of contact time conducted using the AFM Explorer shows that at low and medium loads, the increase in contact time did not seem to affect the measured adhesion forces. At high applied loads a significant increase in adhesion force could be observed as the contact time exceeded 0.1 seconds. The time-dependency of adhesion forces at high loads and high humidities suggests that visco-elastic effects may be a contributing factor to the increase in the adhesion forces under these conditions.

The commercial AFM was used to perform nanoindentation measurements on the material at relative humidities of 0.1% and 65% to measure directly the hardness and the Young's modulus. Both properties reached essentially constant values at indentation depths exceeding 50 nm. Upon changing the relative humidity from 0.1% to 65%, the hardness of polystyrene decreased from 0.11 GPa to 0.08 GPa, and the effective Young's modulus decreased from 1.2 GPa to 1.0
GPa. Although the measured values of hardness and effective modulus seemed to differ from published values, the discrepancy in the hardness value reduced significantly when pile-up effects were taken into account. The measured values of hardness are used to predict the applied load at which plastic yield occurs using the model of Maugis-Pollock. Once the effect of pile-up is accounted for, a value of 1030 nN is predicted. This gives excellent agreement with the experimentally observed transition in adhesion.

The increased ductility of polystyrene at higher relative humidities is explained by the plasticising effect of adsorbed water molecules that dilute the amorphous polymer by diffusion.
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# Table of Contents

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>ABSTRACT</td>
<td>i</td>
</tr>
<tr>
<td>ACKNOWLEDGEMENTS</td>
<td>iv</td>
</tr>
<tr>
<td>TABLE OF CONTENTS</td>
<td>v</td>
</tr>
<tr>
<td>LIST OF FIGURES AND TABLES</td>
<td>xi</td>
</tr>
<tr>
<td>NOMENCLATURE</td>
<td>xix</td>
</tr>
<tr>
<td><strong>CHAPTER 1. INTRODUCTION</strong></td>
<td>1</td>
</tr>
<tr>
<td>1.1 Broad Review</td>
<td>1</td>
</tr>
<tr>
<td>1.2 Aim of Current Research</td>
<td>2</td>
</tr>
<tr>
<td>1.3 Structure of Report</td>
<td>2</td>
</tr>
<tr>
<td><strong>CHAPTER 2. A REVIEW OF THE LITERATURE</strong></td>
<td>4</td>
</tr>
<tr>
<td>2.1 Introduction</td>
<td>4</td>
</tr>
<tr>
<td>2.2 Interparticle Forces</td>
<td>4</td>
</tr>
<tr>
<td>2.2.1 Van der Waals Forces</td>
<td>5</td>
</tr>
<tr>
<td>2.2.2 Electrostatic Forces</td>
<td>6</td>
</tr>
<tr>
<td>2.2.3 Forces with Moisture Present</td>
<td>9</td>
</tr>
<tr>
<td>2.3 Techniques of Force Measurements</td>
<td>15</td>
</tr>
<tr>
<td>2.3.1 Early Attempts</td>
<td>15</td>
</tr>
<tr>
<td>2.3.2 Surface Force Apparatus (SFA)</td>
<td>19</td>
</tr>
<tr>
<td>2.3.3 Atomic Force Microscope (AFM)</td>
<td>20</td>
</tr>
<tr>
<td>2.3.4 Comparison of the AFM and SFA</td>
<td>23</td>
</tr>
<tr>
<td>2.4 Artefacts in AFM</td>
<td>25</td>
</tr>
<tr>
<td>2.4.1 Spring Constant Determination</td>
<td>25</td>
</tr>
<tr>
<td>2.4.2 Working with Particles</td>
<td>30</td>
</tr>
</tbody>
</table>
Table of Contents

2.4.3 Particle Mounting 31
2.4.4 Cantilever and Probe Tip Geometry 32
2.4.5 Mechanical Instability 33
2.4.6 Hysteresis 34
2.4.7 Noise 36
2.4.8 Surface Roughness 37
2.5 Contact Mechanics 40
2.5.1 Johnson-Kendall and Roberts theory (JKR) 40
2.5.2 Derjaguin-Muller and Toporov theory (DMT) 42
2.5.3 Muller analysis 42
2.5.4 Maugis-Pollock theory (MP) 44
2.6 Nanoindentation 45
2.6.1 Measurement of hardness and Young's modulus 46
2.6.2 Hardness determination 48
2.6.3 Young's modulus determination 51
2.6.4 Pile-up influences on hardness and Young's modulus measurement 51
2.7 Polystyrene interactions 53

CHAPTER 3. FORCE MEASURING INSTRUMENTS FOR ADHESION STUDIES 57

3.1 Introduction 57
3.2 Custom-built instrument 57
3.3 Principle of Operation 60
<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.4 Piezo Calibration Technique</td>
<td>61</td>
</tr>
<tr>
<td>3.4.1 Piezo Calibration Results</td>
<td>61</td>
</tr>
<tr>
<td>3.4.2 Effect of Piezo Hysteresis on Acquired Force Curves</td>
<td>63</td>
</tr>
<tr>
<td>3.5 The Atomic Force Microscope (AFM) Explorer</td>
<td>65</td>
</tr>
<tr>
<td>3.5.1 Explorer Scanning Probe Microscope (SPM) head</td>
<td>65</td>
</tr>
<tr>
<td>3.5.2 Piezoelectric ceramic</td>
<td>66</td>
</tr>
<tr>
<td>3.5.3 Feedback loop</td>
<td>67</td>
</tr>
<tr>
<td>3.5.4 Beam alignment</td>
<td>67</td>
</tr>
<tr>
<td>3.5.5 Camera</td>
<td>68</td>
</tr>
<tr>
<td>3.5.6 Data processing software</td>
<td>68</td>
</tr>
<tr>
<td>3.5.6.1 Data acquisition module</td>
<td>68</td>
</tr>
<tr>
<td>3.5.6.2 Image analysis module</td>
<td>69</td>
</tr>
<tr>
<td>3.5.6.3 Data presentation</td>
<td>71</td>
</tr>
<tr>
<td><strong>CHAPTER 4. EXPERIMENTAL TECHNIQUES AND INSTRUMENT CALIBRATION</strong></td>
<td>72</td>
</tr>
<tr>
<td>4.1 Introduction</td>
<td>72</td>
</tr>
<tr>
<td>4.2 Materials</td>
<td>72</td>
</tr>
<tr>
<td>4.3 Preparation of surfaces</td>
<td>72</td>
</tr>
<tr>
<td>4.4 Mounting of particle</td>
<td>73</td>
</tr>
<tr>
<td>4.5 Experimental</td>
<td>76</td>
</tr>
<tr>
<td>4.5.1 AFM non-contact imaging</td>
<td>76</td>
</tr>
<tr>
<td>4.5.2 Point spectroscopy for adhesion and nanoindentation studies</td>
<td>78</td>
</tr>
<tr>
<td>4.5.3 Adhesion studies</td>
<td>79</td>
</tr>
</tbody>
</table>
CHAPTER 5. RESULTS

5.1 Introduction 86
5.2 Experimental Details 87
5.3 Applied load studies 88
   5.3.1 Applied load experiment of a polystyrene particle on polystyrene tablet using the custom-built instrument (PsAl_1) 90
   5.3.2 Applied load experiment of a polystyrene particle on polystyrene tablet using the AFM Explorer (PsAl_2) 94
   5.3.3 Applied load experiment of a polystyrene particle on polystyrene tablet using the AFM Explorer (high loads, PsAl_3) 98
5.4 Adhesion Studies 103
   5.4.1 Polystyrene particle on polystyrene tablet using custom-built instrument (PsAd_1) 103
   5.4.2 Polystyrene particle on polystyrene tablet using custom-built instrument (PsAd_2) 110
   5.4.3 Polystyrene particle on polystyrene tablet using AFM Explorer (PsAd_3) 116
   5.4.4 Polystyrene particle on polystyrene tablet using AFM Explorer (PsAd_4) 123
   5.4.5 Polystyrene particle on polystyrene tablet using AFM Explorer (PsAd_5) 130
   5.4.6 Polystyrene particle on polystyrene tablet using AFM Explorer (PsAd_6) 136
5.5 The effect of contact time 138
5.6 Nanoindentation studies 139
   5.6.1 Nanoindentation of polystyrene tablet using the AFM Explorer at 0.1% RH 143
5.6.2 Nanoindentation of polystyrene tablet using the AFM Explorer at 65% RH

6. STATISCAL ANALYSIS OF RESULTS

6.1 Introduction
6.2.1 T-test for adsorption and desorption cycle for PsAd_1
6.2.2 T-test for adsorption and desorption cycle for PsAd_2
6.2.3 T-test for adsorption and desorption cycle for PsAd_3
6.2.4 T-test for adsorption and desorption cycle for PsAd_4
6.2.5 T-test for adsorption and desorption cycle for PsAd_5
6.2.6 T-test for adsorption and desorption cycle for PsAd_6
6.3 T-test of contact time experiments
6.4 T-test of applied load experiments

7. DISCUSSION

7.1 Introduction
7.2 The effect of relative humidity on the force of adhesion
7.3 The effect of applied load
7.4 The effect of contact time
7.5 Nanoindentation studies of the polystyrene surfaces

8. CONCLUSIONS

8.1 Statement of original problem
8.2 Primary conclusions
8.3. Future work
<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>9. BIBLIOGRAPHY</td>
<td>194</td>
</tr>
<tr>
<td>APPENDIX 1 Piezo Calibration Technique</td>
<td>210</td>
</tr>
<tr>
<td>APPENDIX 2 Student's T-test</td>
<td>212</td>
</tr>
<tr>
<td>APPENDIX 3 Error Analysis</td>
<td>217</td>
</tr>
</tbody>
</table>
### List of Figures and Tables

**Chapter location:**

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>Adhesion between a rigid sphere and a flat surface in the presence of an annulus of pure liquid (Israelachvili, 1992)</td>
</tr>
<tr>
<td>2.2</td>
<td>Typical force curve and its tip movement</td>
</tr>
<tr>
<td>2.3</td>
<td>Typical nanoindentation curve acquired using a sharp conical tip on polystyrene tablet</td>
</tr>
<tr>
<td>2.4</td>
<td>Schematics cross-section of an indentation under load</td>
</tr>
<tr>
<td>2.5</td>
<td>Schematics for the determination of the shape function of a conical tip</td>
</tr>
<tr>
<td>3.1</td>
<td>Photograph of custom-built instrument</td>
</tr>
<tr>
<td>3.2</td>
<td>Side elevation of the force instrument (Tyrrell and Cleaver, 2000)</td>
</tr>
<tr>
<td>3.3</td>
<td>Detail of piezo assembly (Tyrrell and Cleaver, 2000)</td>
</tr>
<tr>
<td>3.4</td>
<td>Example of a piezo calibration curve</td>
</tr>
<tr>
<td>3.5</td>
<td>Piezo displacement versus detector voltage curve without hysteresis correction for silicon nitride probe tip on silicon wafer</td>
</tr>
<tr>
<td>3.6</td>
<td>Piezo displacement versus detector voltage curve with hysteresis correction for silicon nitride probe tip on silicon wafer ($a=0.004$ nmV$^{-2}$, $b=5$ nmV$^{-1}$)</td>
</tr>
<tr>
<td>3.7</td>
<td>Explorer head illustrating the major components of the AFM</td>
</tr>
<tr>
<td>4.1</td>
<td>1-35 μm polystyrene beads compacted at 53 kN (magnification x1000)</td>
</tr>
<tr>
<td>4.2</td>
<td>1-35 μm polystyrene beads compacted at 53 kN (magnification x3500, tilted)</td>
</tr>
<tr>
<td>4.3</td>
<td>Side-view showing particle mounting (not to scale)</td>
</tr>
<tr>
<td>4.4</td>
<td>SEM images of the dimensions of AFM cantilever spring to determine the spring constant</td>
</tr>
<tr>
<td>4.5</td>
<td>SEM image of a mounted polystyrene particle on cantilever</td>
</tr>
<tr>
<td>4.6</td>
<td>Topography scan of polystyrene tablet taken with a 12 μm attached polystyrene particle for applied load studies at low humidities (PsAl_2) with non-</td>
</tr>
</tbody>
</table>
contact imaging

Figure 4.7 Topography scan of polystyrene tablet taken with a bare silicon tip for nanoindentation studies with non-contact imaging

Figure 4.8 Experimental data as exported from the HPVEE data acquisition routine

Figure 4.9 Experimental data with 'zero-force' voltage correction applied

Figure 4.10 Diagram depicting the process of extraction of raw data into force vs true separation curves

Figure 4.11 A force-separation curve analysed from raw experimental data

Figure 4.12 The identification of the starting point for a nanoindentation test

Figure 4.13 Results of a nanoindentation test after the determination of the starting point and the correction of signage

Figure 5.1 Effect of applied load on the force of adhesion of a polystyrene particle interacting with polystyrene tablet measured using the custom-built instrument at various humidities (PsAl_1)

Figure 5.2 Interaction between a 12 μm PS particle and a PS tablet at 14% RH at low applied load (PsAl_1)

Figure 5.3 Interaction between a 12 μm PS particle and a PS tablet at 14% RH at high applied load (PsAl_1)

Figure 5.4 Interaction between a 12 μm PS particle and a PS tablet at 60% RH at low applied load (PsAl_1)

Figure 5.5 Interaction between a 12 μm PS particle and a PS tablet at 60% RH at high applied load (PsAl_1)

Figure 5.6 Effect of applied load on the force of adhesion of a polystyrene particle interacting with polystyrene tablet measured using the AFM Explorer at various humidities (PsAl_2)

Figure 5.7 Interaction between a 12 μm PS particle and a PS tablet at 1% RH at low applied load (PsAl_2)

Figure 5.8 Interaction between a 12 μm PS particle and a PS tablet at 1% RH at high applied load (PsAl_2)
Figure 5.9 Interaction between a 12 μm PS particle and a PS tablet at 65% RH at low applied load (PsAl_2)
Figure 5.10 Interaction between a 12 μm PS particle and a PS tablet at 65% RH at high applied load (PsAl_2)

Figure 5.11 Hysteresis of the adhesion force as a function of applied load between the polystyrene surfaces at 65% RH (PsAl_3)

Figure 5.12 Interaction between a 14 μm PS particle and a PS tablet at 65% RH at low applied load (increasing applied load PsAl_3)
Figure 5.13 Interaction between a 14 μm PS particle and a PS tablet at 65% RH at high applied load (increasing applied load PsAl_3)

Figure 5.14 Interaction between a 14 μm PS particle and a PS tablet at 65% RH at low applied load (decreasing applied load PsAl_3)
Figure 5.15 Interaction between a 14 μm PS particle and a PS tablet at 65% RH at high applied load (decreasing applied load PsAl_3)

Figure 5.16 Effect of increasing RH on the adhesive force of 12 μm PS particle interacting with PS tablet (PsAd_l)
Figure 5.17 Effect of decreasing RH on the adhesive force of 14 μm PS particle interacting with PS tablet (PsAd_l)

Figure 5.18 Interaction between a 12 μm diameter PS particle and a PS tablet at 11% RH in the adsorption sequence (PsAd_1)
Figure 5.19 Interaction between a 12 μm diameter PS particle and PS tablet at 35.4% RH in adsorption sequence (PsAd_1)

Figure 5.20 Interaction between a 12 μm diameter PS particle and PS tablet at 60.2% RH in adsorption sequence (PsAd_1)
Figure 5.21 Interaction between a 12 μm diameter PS particle and PS tablet at 60.6% RH in desorption sequence (PsAd_1)
Figure 5.22 Interaction between a 12 μm diameter PS particle and PS tablet at 40.4% RH in desorption sequence (PsAd_1)
Figure 5.23 Interaction between a 12 μm diameter PS particle and PS tablet at 20.4% RH in desorption sequence (PsAd_1)
Figure 5.24 Interaction between a 12 μm diameter PS particle and PS tablet at 0.9% RH in desorption sequence (PsAd_1)
Figure 5.25 Effect of decreasing RH on the adhesive force of 12 µm PS particle interacting with PS tablet (PsAd_2)

Figure 5.26 Effect of increasing RH on the adhesive force of 12 µm PS particle interacting with PS tablet (PsAd_2)

Figure 5.27 Interaction between a 12 µm diameter PS particle and PS tablet at 60.9% RH in desorption sequence (PsAd_2)

Figure 5.28 Interaction between a 12 µm diameter PS particle and PS tablet at 30.2% RH in desorption sequence (PsAd_2)

Figure 5.29 Interaction between a 12 µm diameter PS particle and PS tablet at 5.8% RH in desorption sequence (PsAd_2)

Figure 5.30 Interaction between a 12 µm diameter PS particle and PS tablet at 1.9% RH in adsorption sequence (PsAd_2)

Figure 5.31 Interaction between a 12 µm diameter PS particle and PS tablet at 34.5% RH in adsorption sequence (PsAd_2)

Figure 5.32 Interaction between a 12 µm diameter PS particle and PS tablet at 70.4% RH in adsorption sequence (PsAd_2)

Figure 5.33 Effect of increasing RH on the adhesive force of 10 µm PS particle interacting with PS tablet (PsAd_3)

Figure 5.34 Effect of decreasing RH on the adhesive force of 10 µm PS particle interacting with PS tablet (PsAd_3)

Figure 5.35 Interaction between a 10 µm diameter PS particle and PS tablet at 2.1% RH in the adsorption sequence (PsAd_3)

Figure 5.36 Interaction between a 10 µm diameter PS particle and PS tablet at 35% RH in the adsorption sequence (PsAd_3)

Figure 5.37 Interaction between a 10 µm diameter PS particle and PS tablet at 64.6% RH in the adsorption sequence (PsAd_3)

Figure 5.38 Interaction between a 10 µm diameter PS particle and PS tablet at 63.9% RH in the desorption sequence (PsAd_3)

Figure 5.39 Interaction between a 10 µm diameter PS particle and PS tablet at 35% RH in the desorption sequence (PsAd_3)
Figure 5.40 Interaction between a 10 μm diameter PS particle and PS tablet at 5.6% RH in the desorption sequence (PsAd_3)

Figure 5.41 Effect of increasing RH on the adhesive force of 10 μm PS particle interacting with PS tablet (PsAd_4)

Figure 5.42 Effect of decreasing RH on the adhesive force of 10 μm PS particle interacting with PS tablet (PsAd_4)

Figure 5.43 Interaction between a 10 μm diameter PS particle and PS tablet at 9.9% RH in the desorption sequence (PsAd_4)

Figure 5.44 Interaction between a 10 μm diameter PS particle and PS tablet at 39.3% RH in the adsorption sequence (PsAd_4)

Figure 5.45 Interaction between a 10 μm diameter PS particle and PS tablet at 66.7% RH in the adsorption sequence (PsAd_4)

Figure 5.46 Interaction between a 10 μm diameter PS particle and PS tablet at 65% RH in the desorption sequence (PsAd_4)

Figure 5.47 Interaction between a 10 μm diameter PS particle and PS tablet at 31.2% RH in the desorption sequence (PsAd_4)

Figure 5.48 Interaction between a 10 μm diameter PS particle and PS tablet at 10% RH in the desorption sequence (PsAd_4)

Figure 5.49 Effect of increasing RH on the adhesive force of 10 μm PS particle interacting with PS tablet (PsAd_5)

Figure 5.50 Effect of decreasing RH on the adhesive force of 10 μm PS particle interacting with PS tablet (PsAd_5)

Figure 5.51 Interaction between a 10 μm diameter PS particle and PS tablet at 11.3% RH in the adsorption sequence (PsAd_5)

Figure 5.52 Interaction between a 10 μm diameter PS particle and PS tablet at 40% RH in the adsorption sequence (PsAd_5)

Figure 5.53 Interaction between a 10 μm diameter PS particle and PS tablet at 60.6% RH in the adsorption sequence (PsAd_5)

Figure 5.54 Interaction between a 10 μm diameter PS particle and PS tablet at 65.1% RH in the desorption sequence (PsAd_5)
Figure 5.55 Interaction between a 10 μm diameter PS particle and PS tablet at 46% RH in the desorption sequence (PsAd_5)

Figure 5.56 Interaction between a 10 μm diameter PS particle and PS tablet at 16% RH in the desorption sequence (PsAd_5)

Figure 5.57 Effect of increasing RH on the adhesive force of 10 μm PS particle interacting with PS tablet without topographical measurements (PsAd_6)

Figure 5.58 The effect of contact time on the adhesion forces of polystyrene surfaces at 65% RH at different applied loads

Figure 5.59 SEM images of probe tip before and after nanoindentation tests at 0.1% RH

Figure 5.60 SEM images of probe tip before and after nanoindentation tests at 65% RH

Figure 5.61 Maximum contact depth of nanoindentations conducted at 0.1% RH versus maximum load

Figure 5.62 Hardness of cross-linked polystyrene at 0.1% RH evaluated using the Oliver-Pharr procedure versus contact depth

Figure 5.63 Effective Young's modulus of cross-linked polystyrene at 0.1% RH evaluated using the Oliver-Pharr procedure versus contact depth

Figure 5.64 Maximum contact depth of nanoindentations conducted at 65% RH versus maximum load

Figure 5.65 Hardness of cross-linked polystyrene at 65% RH evaluated using the Oliver-Pharr procedure versus contact depth

Figure 5.66 Effective Young's modulus of cross-linked polystyrene at 65% RH evaluated using the Oliver-Pharr procedure versus contact depth

Figure 6.1 Student's t-test analysis results on adsorption for a 12 μm PS particle interacting on PS tablet (PsAd_1)

Figure 6.2 Student's t-test analysis results on desorption for a 12 μm PS particle interacting on PS tablet (PsAd_1)

Figure 6.3 Student's t-test analysis results on adsorption for a 12 μm PS particle interacting on PS tablet (PsAd_2)

Figure 6.4 Student's t-test analysis results on desorption for a 12 μm PS particle
Figure 6.5 Student's t-test analysis results on adsorption for a 10 μm PS particle interacting on PS tablet (PsAd_2)

Figure 6.6 Student's t-test analysis results on desorption for a 10 μm PS particle interacting on PS tablet (PsAd_2)

Figure 6.7 Student's t-test analysis results on adsorption for a 10 μm PS particle interacting on PS tablet (PsAd_3)

Figure 6.8 Student's t-test analysis results on desorption for a 10 μm PS particle interacting on PS tablet (PsAd_3)

Figure 6.9 Student's t-test analysis results on adsorption for a 10 μm PS particle interacting on PS tablet (PsAd_4)

Figure 6.10 Student's t-test analysis results on desorption for a 10 μm PS particle interacting on PS tablet (PsAd_4)

Figure 6.11 Student's t-test analysis results on adsorption for a 10 μm PS particle interacting on PS tablet (PsAd_5)

Figure 6.12 Student's t-test analysis for results on the effect of contact time on the forces of adhesion between a single polystyrene particle interacting on a PS tablet at 65% RH

Figure 6.13 Student's t-test analysis for results on the effect of applied load on the forces of adhesion between a single polystyrene particle interacting on a PS tablet at 1% RH, 35% RH and 65% RH

Figure 6.14 Student's t-test analysis for results on the effect of applied load on the forces of adhesion between a single polystyrene particle interacting on a PS tablet at 65% RH.

Figure 7.1 Comparison of adhesion forces from adsorption data acquired from the AFM and custom built instrument

Figure 7.2 Comparison of predicted and measured adhesion forces of a 12 μm polystyrene particle interacting with a polystyrene substrate using the custom-built instrument

Figure 7.3 Comparison of predicted and measured adhesion forces of a 10 μm polystyrene particle interacting with a polystyrene substrate using the AFM Explorer

Figure 7.4 Evaluation of yield point of a 12 μm polystyrene particle interacting on polystyrene substrate calculated using a JKR and MP contact mechanics theories at
65% RH

Figure 7.5 Hardness of cross-linked polystyrene at 65% RH versus contact depth 182

Figure A1 schematic diagram showing calibration of the sample piezo 213

Table 2.1 Non-retarded Van der Waals' interaction free energies between bodies of different geometries (Garbassi et al., 1998) 6

Table 2.2 Values of Young's modulus for silicon nitride 26

Table 3.1 Piezo model parameters 63

Table 4.1 Equilibrium study on polystyrene surfaces 80

Table 7.1 Mechanical properties of cross-linked polystyrene evaluated by nanoindentation studies 184

Table 7.2 The effects of pile-up on the evaluated hardness and effective Young's modulus at 0.1% RH 186
Table 7.3 The effects of pile-up on the evaluated hardness and effective Young's modulus at 65% RH 186

Table 7.4 The effects of pile-up on the evaluated hardness, effective Young's modulus and load required for yield at 0.1% RH and 65% RH 187

Table A1 Value of degrees of freedom for the evaluation of Student's T-test 215

Table A2 Student's T-test for adsorption data of a 12 μm PS particle interacting on PS tablet for Ps_Ad3 216

Table A3 Equations used for error analysis 219
Table A4 Error analysis of spring constant determination 220
### NOMENCLATURE

- **r**: Centre-centre distance between atoms (m)
- **D**: Sphere-sphere or sphere-flat separation (m)
- **A**: Hamaker constant (J)
- **M_W**: Molecular weight (kg.kmol⁻¹)
- **ρ**: Density (kg.m⁻³)
- **R**: Gas constant (J.K⁻¹.mol⁻¹)
- **R**: Particle radius (m)
- **T**: Temperature (K)
- **P_L**: Laplace pressure (N.m⁻²)
- **P_0**: Saturated vapour pressure (N.m⁻²)
- **γ**: Surface tension of liquid (N.m⁻¹), (J.m⁻²)
- **γ_LV**: Liquid/vapour surface tension (N.m⁻¹), (J.m⁻²)
- **γ_SL**: Solid-liquid interfacial free energy (J.m⁻²)
- **θ**: Half-angle of indenter tip (degrees)
- **θ**: Solid-liquid contact angle (degrees)
- **φ**: Half-filling angle (degrees)
- **E**: Young's modulus (N.m⁻²)
- **w**: Width of cantilever (m)
- **l**: Length of cantilever (m)
- **t**: Thickness of cantilever (m)
- **k**: Spring constant of cantilever (N.m⁻¹)
- **M_1**: Mass of sphere applied to cantilever (kg)
- **v_0**: Unloaded resonant frequency (kHz)
- **v_1**: Loaded resonant frequency (kHz)
- **M_p**: Mass of pendulum (kg)
- **g**: Acceleration due to gravity (m.s⁻²)
- **Δz_p**: Displacement of pendulum (m)
- **L**: Pendulum length (m)
- **Δz_c**: Cantilever displacement due to displacement of pendulum (m)
- **Ω**: Deflection calibration constant (-)
- **ω_0**: Resonant frequency of cantilever (kHz)
- **χ_0**: Amplitude of cantilever (m)
\( m \)  Effective mass of cantilever  
\( k_B \)  Boltzmann's constant  
\( a \)  Radius of contact area  
\( P \)  Applied load  
\( \nu \)  Poisson's ratio  
\( w_A \)  Thermodynamic work of adhesion  
\( P_s \)  Pull-off force/Adhesion force  
\( z_o \)  Interatomic spacing  
\( Y \)  Yield strength  
\( H \)  Hardness  
\( h_f \)  Final depth of indentation after unloading  
\( h_e \)  Elastic displacement of the surface after unloading  
\( h \)  Total depth of indentation  
\( h_e \)  Contact depth  
\( h_{max} \)  Maximum depth of indentation  
\( S \)  Unloading stiffness  
\( S \)  Piezo displacement  
\( P_{max} \)  Peak indentation load  
\( A \)  Projected area of contact  
\( E_r \)  Reduced Young's modulus  
\( x \)  Deflection of cantilever  
\( a \)  Piezo hysteresis coefficient  
\( B \)  Piezo linear expansion coefficient  
\( V \)  Applied potential  
\( V_m \)  Maximum applied potential  
\( RH \)  Relative humidity
1.1 BROAD REVIEW

The adhesion of particles and the removal forces from substrates is of great technological importance and scientific interest. Examples of the technological uses of particle adhesion include the fabrication of semiconducting devices, controlled movement of toner in xenography, absorption of site-specific medications in pharmacology, adhesion of paints and inks to substrates, adhesion of dust to precision optics and the controlled use of pesticides and fungicides in agriculture. In addition to these diverse applications, the study of particle adhesion facilitates the basic understanding of the interactions between materials under investigation at a fundamental level without complications from confounding factors. The study of adhesion between materials at small length scales has been made possible with the advances of high resolution force measuring instruments such as the Surface Force Apparatus developed by Israelachvili and co-workers in the 1970's the and the Atomic Force Microscope by Binnig et. al. (1986).

In order to fully understand the adhesion phenomena between materials, the effects of parameters such as relative humidity, applied load and contact time must be investigated. It has been long established that adsorption of moisture greatly influences the adhesion properties of particulate solids (McFarlane and Tabor, 1950; Coehlo and Harnby, 1978; Bracken, 1997). The extent of the influence of relative humidity depends on the chemical and physical properties of the material and the system temperature. The presence of adsorbed moisture modifies the interactions between the particles and therefore has an effect on a number of process operations, such as fluidization, tabletting, agglomeration, conveying of powders and hopper flow (Tyrell, 2000). The effect may be beneficial or detrimental depending on when and where it occurs within a process.

Even though polystyrene is a common polymer used in many industrial applications from insulation to paint, the interactions and behaviour of polystyrene particles are not well known, in particular the effects of relative humidity, applied load and contact
time on its adhesion properties have not been investigated in the past. It is therefore
the main objective of this project to quantify the importance and extent of influence of
these parameters on the adhesion of polystyrene.

The characterisation of the interactions between polystyrene surfaces is part of a
larger project sponsored by EPSRC and ICI plc., which aims to identify the effects of
interparticle interactions on the strength of aggregates and agglomerates by Distinct
Element Method modelling and to analyse their disintegration and dispersion when
they are subjected to various types of mechanical stresses, such as impact and slow
shear deformation as prevailing in process applications.

1.2 AIMS OF CURRENT RESEARCH

The interactions between individual polystyrene particles and a polystyrene substrate
are characterised in this project using a custom-built force instrument and a
commercial Atomic Force Microscope Explorer (AFM). The force of adhesion, which
holds the two surfaces together, is measured using the two instruments and the effects
of relative humidity, applied load and contact time are extensively studied. The
primary aim of the project is to characterise the change in behaviour of the interacting
polystyrene surfaces as a consequence of changes in the above parameters. The
observations are interpreted in terms of established contact mechanics theories. To
further understand the behaviour of the interacting species, the surface mechanical
properties of polystyrene particles are independently measured by conducting
nanoindentation studies using the Atomic Force Microscope.

The project demonstrates the immense capability of AFM by bringing together AFM
measurement of adhesion, nanoindentation and topography.

1.3 STRUCTURE OF REPORT

A comprehensive literature review is presented in Chapter 2 on relevant topics such as
various interparticle force mechanisms which cause adhesion. The techniques of
measuring these forces and the relevant knowledge on contact mechanics and
nanoindentation will be presented and discussed.
The third chapter of the report details the operation and the layout of the custom-built force instrument, which is used to conduct part of the experimental studies. The main operating components of the Atomic Force Microscope Explorer (AFM Explorer) will also be discussed.

The experimental techniques and the methodology behind instrument calibration for both the custom-built force instrument and the commercial Atomic Force Microscope will be presented in the fourth chapter together with the material preparation techniques.

The fifth chapter describes all the results from the various experimental studies conducted using individual polystyrene particles interacting with a polystyrene substrate. The effects of relative humidity, applied load and contact time will be presented in this chapter. Results of nanoindentation studies on the polystyrene surfaces will also be described and discussed here.

Chapter 6 details the statistical analysis performed on all the experimental results to evaluate the errors associated with the data.

In the seventh chapter, the experimental results shown in the previous chapter will be discussed and the various mechanisms which may explain the behaviour of the interacting polystyrene surfaces will be described.

The main conclusions drawn from the experimental results will be presented in Chapter 8 along with recommendations for future work.
CHAPTER 2 LITERATURE REVIEW

2.1 INTRODUCTION

Adhesion between colloidal particles and a solid surface is of fundamental importance in many industrial and commercial contexts; e.g., foods, pigments/paints, ceramics, pharmaceuticals, photography and air pollution control. Although adhesion is encountered in many phenomena in everyday life, the mechanisms and factors governing it are complex and have raised substantial scientific issues.

It has been long established that interparticle forces such as van der Waals forces play a dominant role in adhesion, especially when the particle size falls below 100 µm, when the adhesive force tends to exceed the particle weight. The force measured between fine particles is very small (10 nN→10 µN) and acts over a comparatively short distance (up to several hundred nanometers). Sensitive instrumentation is therefore required to detect these forces and displacements.

In order to improve the performance of powders during processing and use, advances in the understanding of microscale phenomena must be made (Clift, 1994). This is endorsed by Pollock (1994) who remarks upon an urgent need for the pursuit of direct force measurements at the level of an individual particle. These comments can be summarised by the need to be less reliant on the empirical relationships and their associated limitations. An understanding on a more fundamental level is advocated.

2.2 INTERPARTICLE FORCES

In this section, the various force mechanisms which contribute to adhesion are reviewed. The theoretical approaches to these mechanisms are described and experimental evidence is also discussed.

The primary interparticle force mechanisms of potential relevance are:
2.2.1 Van der Waals Forces

Van der Waals forces essentially result from the London (dispersion), Keesom (orientation) and Debye (induction) interaction energies. The effect of these interaction energies is a net attraction between the dipoles of individual atoms. All three interaction energies decay as $r^{-6}$, where $r$ is the centre-centre distance between the atoms (Israelachvili, 1992).

When the time for electromagnetic radiation to propagate between molecules becomes comparable to the lifetime of the fluctuating dipoles, the correlation between nearby dipoles is weakened and the attractive energy is reduced, ultimately decaying as $r^{-7}$ instead of $r^{-6}$. This weakening of the correlation is called retardation.

In 1937, Hamaker computed the van der Waals interaction between two particles of a condensed phase by linearly superimposing the atom-atom interactions. This ignores the effect of intervening atoms on the correlation between two interacting dipoles. In 1955, Lifshitz devised a continuum theory to calculate the van der Waals interaction between condensed phases. For the non-retarded interactions between two half spaces, both theories predict that the interaction potential per unit area decays as $D^{-2}$, where $D$ is the separation distance. The main difference between the Hamaker and Lifshitz approaches lies in the prediction of the proportionality constant $A$, called the Hamaker constant. The van der Waals approximation for bodies of different geometries is summarised in Table 2.1:
Table 2.1 Non-retarded Van der Waals' interaction free energies between bodies of different geometries (Garbassi et al., 1998)

<table>
<thead>
<tr>
<th>System</th>
<th>Geometries</th>
<th>Van der Waals Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Sphere-surface</td>
<td>( W = -\frac{4A}{6D} )</td>
</tr>
</tbody>
</table>
|            | Two cylinders    | \( W = \frac{AL}{12\sqrt{2D^{3/2}}} P \)  
\[ P = \left( \frac{R_1 R_2}{R_1 + R_2} \right)^{1/2} \] |
|            | Crossed cylinders| \( W = A\sqrt{\frac{R_1 R_2}{6D}} \) |
|            | Two surfaces     | \( W = \frac{-A}{12\pi D^2} \) per unit area |

### 2.2.2 Electrostatic forces

Electrostatic forces potentially contribute to particle adhesion both in air and in liquids.
Electrostatic forces in air

Two solids in contact with one another, in general, charge each other electrostatically. There is abundant literature on the experimental part of this subject; for pertinent reviews, reference is made to Loeb (1958) and Montgomery (1959).

Electrostatic forces may arise from a Coulombic interaction. If a charged particle is brought into contact with an uncharged surface, the charged particle induces an equal charge, but of opposite sign, at an equal distance from the surface. This so-called image charge leads to an attractive force.

Experiments conducted by Schnabel (1969) on polymer particles and semiconductors demonstrated that electrostatic forces might be a dominant source of adhesion in such systems. Derjaguin et al. (1968/1969) estimated the contribution of electrostatic forces on the adhesion of polyvinyl chloride particles on steel plates in air by measuring the force of adhesion and the charge of the double layer arising upon contact. In the systems investigated, the adhesive force and the charge after separation increased with the diameter of the particles in the range of 2 to 30 μm, according to a power law with an exponent close to 2. Using an ultracentrifuge method, Cross (1979) studied the effect of particle charge on the adhesion of 20 μm calcium tungstate powder particles and showed that a significant force is required to detach these particles when charged using corona charging techniques, compared to neutral particles. Since the specific charge of these particles due to different charging mechanisms has not been reported, it is difficult to explain the observed variation. Uber et al. (1982) used a specially designed apparatus to measure the adhesive force between small particles and the charge transferred during that contact. Adhesive forces of $10^{-9}$ N and charges of $10^{18}$ C can be measured using this system. The results showed that charge transfer was only tens of electrons with the exception of gallium arsenide. The implication of this work is that electrostatic forces do not appear to be an important adhesive mechanism because no correlation has been observed between adhesive force and charge transfer.
In water and in other media, which favour electrolytic dissociation, particles are usually charged although the suspension as a whole is electroneutral. A charge opposite to that of the particles is carried by small ions in the solution and these form a diffuse electric double layer around each particle. When colloid particles approach one another, the interaction of these double layers causes repulsion. For electrically stabilized colloids in a liquid, the combined influence of van der Waals attraction and electrostatic repulsion has to be considered (Verwey and Overbeek, 1948; Derjaguin and Landau, 1941; Overbeek, 1984). This consideration has resulted in a theory known as DLVO theory that describes the relationship of force versus separation for such systems. Irrespective of the size or shape of the particles, the common feature is that attraction decays as an inverse first or higher power of the distance between the two particles, or particle-surface, \( D \), and the repulsion decays as an exponential function of this distance. Therefore, the attraction is always greater at short distances \((-1/D \to \infty)\) and at large distances \((1/D^n \to \exp(-\kappa D))\), but at intermediate distances the repulsion may be greater. The validation of the DLVO theory has been investigated by many, using AFM measurements such as Parker et al. (1989) with mica surfaces, Larson et al. (1993) using titanium oxides surfaces, Ducker et al. (1992) using silica surfaces and Senden et al. (1994) using a silicon nitride sample. However, Parker et al. (1989) have shown that the measured forces between mica deviate from the DLVO theory at short separations due to a hydration repulsion. This observation was confirmed from experiments by Ducker et al. (1992) on silica surfaces when the measured forces were found to be in good agreement with the DLVO theory only at separations above 3 nm. For an extensive review on the validations and discussions on the DLVO theory, the work of Hiemenz (1977), and Swanton (1995) are recommended.

Whilst we are not primarily concerned with particles in liquids, the role of double layer repulsion is potentially relevant to particles contacting through adsorbed liquid layers. It is generally accepted that the presence of immobile layers of adsorbed moisture eliminates or at least greatly reduces the effect of Coulombic forces between the particles. Zimon (1982) states that in the presence of moisture in the gap between
the contiguous bodies, electrostatic forces cannot exist. A wide range of published experimental evidence supports this. Tsuyuguchi _et al._ (1994) showed that the presence of an adsorbed water layer enhanced both the surface diffusion and dissipation of charge for contact electrified charges on a thin SiO₂ film in air. Wan _et al._ (1992) measured adhesive forces and surface charges for surfaces of mica and silica and observed high values of adhesion during experiments in dry nitrogen when the relative humidity was between 1 and 2%. Upon increasing the RH slightly (while maintaining the RH < 10%) the adhesive force fell by about an order of magnitude to a value that corresponded to capillary bonding. The drop in adhesion coincided with a decrease in the time taken for electrical charge dissipation from the surfaces; the exponential decay time constant fell by about two orders of magnitude. Turner and Balasubramanian (1974) calculated the contribution of electrical forces to the strength of an assembly of lightly compacted, small (45 - 90 μm diameter) glass beads for humidities ranging from 19 - 38%. The authors have showed both positive and negative charges to be present on the glass surface and calculated the electrical contribution to bulk cohesion for conducting and non-conducting particles based on typical surface charge densities. They find the contribution to be, at most, about 6% of the observed value based on the measured tensile strength of the sample bed.

### 2.2.3 Forces with Moisture Present

The presence of moisture on the surface of particles can significantly affect the force-separation relationship and the adhesion between the particles. The moisture can arise either from adsorption from the surrounding air, it can be intentionally added to act as a binder, or it can be present as a residue from filtration or incomplete drying.

Established wisdom (e.g. Zimon, 1982) identifies two main mechanisms through which moisture influences the interparticle forces, depending on the quantity of water present, i.e. the thickness of the water layer on the surface. For thin water layers, the mobility of the layer is greatly inhibited, and the water effectively acts as an agent to fill in surface asperities, increasing the contact area and thus increasing the force required for separation.
Conversely, when the surface layer is sufficiently thick to cover all the asperities, the film readily forms a complete capillary bridge at the particle-particle contact point. This leads to a notable increase in adhesion due to the additive effects of the reduced pressure in the capillary, the surface tension around the bridge perimeter and the solid-solid interaction. The latter contribution can be a significant component of the adhesion according to Barthel et al. (1996).

There is some ambiguity about the film thickness at which liquid mobility occurs. NMR relaxation studies (Adamson, 1990) suggest that water molecules exhibit mobility once monolayer coverage is exceeded. Other studies on forces between hydrophilic particles by Zimon (1982) suggest that capillary forces are significant once a relative humidity of 65% is reached. In reality, capillaries can form at very low humidities due to capillary condensation. These capillaries do not usually contribute significantly to adhesion because they act at isolated contact points between asperities. It is not until these asperities are engulfed that capillary bridge forces increase dramatically. Surface roughness is therefore a significant parameter and must be considered in conjunction with the quantity of adsorbed water. The affinity of the surface for water, i.e., the hydrophobicity or hydrophillicity also significantly affects the effect of relative humidity on the force of adhesion.

A technique was developed by Harnby et al. in 1996 for measuring the adhesion force between an array of individual particles and a flat surface. Several thousand particles either glass ballotini or sand were positioned in the apertures of an electroformed microsieve. The adhesive force between the array and a flat surface of brass, glass or stainless steel was measured to within 0.1 mg using a top pan balance. The adhesion forces acquired from this technique will be later discussed in Section 2.3.1. However, it is worth mentioning that for all the systems tested, the authors observed an increase in adhesion with an increase in relative humidity. The critical value of relative humidity at which adhesion increased markedly lay between 60% and 80%, which is broadly in agreement with the observations of Zimon (1982).

McFarlane and Tabor (1950) performed a number of experiments to measure the adhesion between surfaces of glass, platinum and silver. The effect of relative
humidity on the adhesion of glass surfaces showed that maximum adhesion was reached when the relative humidity was 88%; with a glass sphere on a polished platinum surface maximum adhesion occurred between 93 and 100% humidity. It was shown that the thickness of the water film and the adhesion of glass surfaces both increased rapidly at humidities greater than 90%.

Zimon (1969) found that the force of adhesion of 20-200 μm spherical dust particles to a glass surface remained approximately the same in the 5 to 65% relative humidity (RH) ranges. Above 65% RH, the adhesion increased with RH and the increase was attributed to the onset of capillary condensation. At an RH close to 100%, the force of adhesion decreased. This was explained by the disjoining pressure of the liquid film in the gap, resulting in a repulsive force and an associated increase in the distance between the particle and the substrate. Zimon proposed that this would be a good method for determining disjoining pressure. The existence of a disjoining pressure may well be the explanation for the peak adhesive force at 88% RH, as reported by McFarlane and Tabor (1950). At maximum adhesion, the total adhesive force obeyed Eqn. (2.4). According to Zimon, this was also shown by Burson et al. (1963) for glass spheres of 0.01 to 0.1 cm radius under conditions where the particles are initially pressed against a brass surface. In general, the difference between capillary forces and the other contributions to the adhesive force are particularly appreciable for particles more than 10 μm in diameter (Zimon 1982). The differences are less when the particle size diminishes (Zimon, 1982). The effect of surface tension predicted by Eqn. (2.4) was substantiated by adhesion measurements with spherical glass beads (30 to 70 μm in diameter) on untreated glass, hydrophilized and hydrophobized glass in vacuo, and in an atmosphere saturated with water, acetone, and carbon tetrachloride vapour.

Chikazawa et al. (1984) studied the effect of adsorbed water vapour on glass beads. The authors measured the changes in adhesion force with the amount of adsorbed water vapour and found that the adhesion force under low water vapour pressure (P/P₀< 0.5) can be ascribed to hydrogen-bonds owing to a low coverage of water molecules. An increase of adhesion in the high vapour pressure region (P/P₀>0.6) is due to a transformation from hydrogen-bond formation to liquid bridge formation.
Chapter 2 Literature Review

The transformation is considered to be generated by the change in physical properties of the water layer with the adsorbed amount.

The influence of relative humidity on the adhesion of lactose monohydrate particles and salmeterol xinafoate particles has been investigated by Podczeck et al. (1997). Condensed moisture was found to result in strong irreversible solid bridge bonds, or in weak solid bridge bonds that are of comparable strength to Lifshitz-van der Waals forces obtained under conditions of low RH up to 35%. The effect was found to be dependent on the structure of the substrate surface, the solubility of the particles adhered, and the solubility of the surface material. Relative humidities greater than 75% resulted in strong irreversible forces acting at the interface of the particles. Below this humidity level, capillary forces could be removed by storing the mixtures at very low relative humidity of about 5% for at least 72 hours.

Particle interaction forces, induced by wetting and the adherence of wet powders to hard surfaces, was found to reduce by a factor of 2 when the hydophobicity of the particles was increased and a reduction of adhesion by a factor of 25 to 30 was observed when the hydophobicity of the hard surface was increased (Metskevich and Nerpin, 1967). Löffler (1968) found that the adhesion of quartz particles to polyester increased by a factor of 1.5 when the RH was increased from 70% to 90%. In the case of a polyamide substrate, adhesion increased by a factor of 2.5 when the RH rose from 20% to 50%, but no further increase in adhesion could be detected between 50% to 90% RH. On glass, a continuous increase in adhesion of the quartz particles was found from 20% to 90% RH.

The effect of adsorbed moisture acting as a plasticizer has been demonstrated by Iida et al. (1992) and hence increases the adhesion force via increasing the contact area between the contiguous bodies due to enhanced plastic deformability. Adsorbed water can lead to the formation of solid bridges between contacting particles if dissolution of the material occurs, followed by subsequent recrystallisation as a result in changes in relative humidity of temperature. The forces generated in solidifying liquid bridges between two small particles were investigated by Tardos and Gupta (1996). The authors found that the solid bridges exerted large attractive forces which corresponded
to two hundred to four hundred times the weight of the bridge. The formation of solid bridges in particulate material may be extremely problematic in industrial applications as it leads to powder caking and severely reduces the flowability of the material.

A classical theoretical expression for the magnitude of capillary forces is described by the Laplace-Kelvin theory. The vapour pressure of the liquid bridge can be related to the surface tension of the liquid, the absolute temperature and the principal radii of the curvature of the bridge by the Kelvin equation, i.e.

\[
\frac{P}{P_o} = \exp\left[-\frac{M_w P_L}{\rho R T}\right]
\]

Eqn(2.1)

where \( M_w \) is the liquid molecular weight, \( \rho \) is the liquid density, \( R \) is the gas constant, \( T \) is the absolute temperature and \( P_L \) is the Laplace pressure in the liquid. \( P_L \) is given by the Laplace equation, i.e.

\[
P_L = \gamma \left(\frac{1}{r_1} + \frac{1}{r_2}\right)
\]

Eqn(2.2)

Here, \( \gamma \) is the surface tension of the liquid and \( r_1 \) and \( r_2 \) are the principal radii of curvature of the liquid as defined in Figure 2.1. The validity of the Kelvin equation has been tested and verified by various investigators such as Cross and Picknett (1963) and Fisher and Israelachvili (1979, 1981).

Figure 2.1 Adhesion between a rigid sphere and a flat surface in the presence of an annulus of pure liquid (Israelachvili, 1992)
Fisher and Israelachvili (1981) expanded the Laplace-Kelvin theory to describe the adhesion between a rigid sphere and a flat surface in the presence of an annulus of pure liquid (see Figure 2.1) using the following equations

\[
F = F(P_L) + F(s-s) + F(\gamma_{LV}) \quad \text{Eqn}(2.3)
\]

\[
F(P_L) = 4\pi R\gamma_{LV} \cos \theta \quad \text{Eqn}(2.4)
\]

\[
F(s-s) = 4\pi R\gamma_{SL} \quad \text{Eqn}(2.5)
\]

\[
F(\gamma_{LV}) = 2\pi R\gamma_{LV} \sin \phi \sin(\theta + \phi) \quad \text{Eqn}(2.6)
\]

Here, \(F(\Delta P)\) is the force due to the Laplace pressure \(P_L\), \(F(s-s)\) is the solid-solid interaction which occurs across \(n\)-layers of condensed fluid molecules trapped between the surface when they are brought into contact, \(F(\gamma_{LV})\) is the resolved force due to the liquid/vapour surface tension \(\gamma_{LV}\), \(R\) is the radius of the sphere, \(\theta\) is the solid-liquid contact angle, \(\gamma_{SL}\) is the solid-liquid interfacial free energy and \(\phi\) is as shown in Figure 2.1. Wanless and Christenson (1994) comment that the \(F(s-s)\) is negligible when the surfaces are separated by more than two layers of liquid molecules and the final term, \(F(\gamma_{LV})\), can also be neglected when the radius of the sphere \(R\) greatly exceeds the neck radius, so that \(\phi\) is small. Hence, \textit{Eqn} (2.3) reduces to \textit{Eqn} (2.4) for a reasonable approximation of the adhesion force in the presence of adsorbed moisture. For a perfectly wetted system, the \(\cos \theta\) term becomes unity as \(\theta \rightarrow 0\).

Several other theories for calculating capillary forces are also proposed e.g., O'Brien and Hermann (1973), Gillespie and Settineri (1967) and Metskevich and Nerpin (1967). These are refinements to the above model which are more relevant to systems in which significant quantities of liquid are present.
2.3 TECHNIQUES OF FORCE MEASUREMENTS

A number of different techniques and methods have been used over the years to quantify the forces between individual particles and between a particle and a surface. The aim of this section is to review and briefly describe the relevant methods used in the past and present to measure interparticle forces. Atomic force microscopy is discussed in greater detail, as this is the predominant technique used in the current work.

2.3.1 Early attempts

Attempts to quantify the forces between particles started as early as 1928 when Tomlinson measured the force of adhesion between fibres or spheres of glass to determine the index of the decay law. Tomlinson’s experimental results were inconclusive but he made several technical advances which are still in current use such as the cross-cylinder geometry, now widely used in the application of the surface force apparatus (see Section 2.3.2). Bradley (1932), continuing the work of Tomlinson (1928), developed an apparatus for measuring the adhesion between spheres of unequal size. This instrument utilised a microscope to detect deflection, and a quartz spring to determine the force. Bradley reported the adhesion of two quartz spheres were independent of whether the measurement was made in a vacuum or air. Experiments were also conducted with freshly fused sodium pyroborate spheres. The adhesion forces measured in vacuum were observed to drop to about a third of their value measured in ambient air. The high value of adhesion in air was attributed to the adsorption of water. Rayleigh (1936) examined the force required to separate glass surfaces which were in “optical contact”. One edge was peeled away from the other surface using a weight. The separation of the surfaces during this process could be followed from the interference fringes produced in the gap of the surfaces. This represents the first work to measure both the surface separation and the force concurrently, and led the way for many attempts to quantify attractive forces and distance dependence in order to test the theories of London (1930), Hamaker (1937) and later Lifshitz (1956).
McFarlane and Tabor (1950), Howe et al. (1955) and Hotta et al. (1974) used a pendulum-type apparatus to measure adhesion between particles. Although the sensitivity of the apparatus was advanced for its time, it still limited the study to the use of relatively large particles of 1 mm in diameter or above.

A method using a centrifuge to study the adhesion of many particles at a time was popular amongst many investigators including Beams et al. (1955); Gillespie and Rideal (1955); Larsen (1958); Kordecki et al. (1960) and Zimon and Derjaguin (1963). In this method, the substrate is covered with the particles and is centrifuged with an increasing angular velocity. The number and size of those particles which are detached is recorded. This procedure is continued at increasing angular velocities until all particles are removed. The results may then be expressed as the fractional percentage of particles adhering to the substrate before and after the centrifuge process, as a function of the applied acceleration. By multiplication of the acceleration by the mass of the particles the distribution function versus the adhesive force is obtained. A disadvantage of this method is that the maximum acceleration that can be attained is of the order of $10^5$ g to $10^6$g. Consequently, the technique is only suitable for use with particles over 1 µm in diameter and of high density, e.g. metals.

The centrifuge method has been modified and improved by Bohme et al. (1964, 1965), Staniforth et al. (1981) and Podczeck et al. (1995a, 1995b). The particles used in these experiments vary from 20-40 µm. The new ultracentrifuge method allows the application of about 3-fold increase acceleration, which provides the centrifugal force necessary for detachment of micronized particles from the surfaces. A set of adapters for a vertical rotor allows for unlimited measurement of angled detachments.

These centrifuge techniques are only capable of giving a statistical inference of the adhesion forces of the material in bulk; the individual adhesion forces are not obtainable. Furthermore, there is no facility to study issues such as the force-separation relationship or the effect of strain rate on adhesion.

A vibration method has been employed by a number of investigators (Zimon, 1969; Larsen, 1958; Derjaguin and Zimon, 1961; Walker and Fish, 1966), where the force
of removal for particles on a vibrating surface is obtained by means of an ultrasonic system generating oscillations at frequencies of 10 to 20 kHz. The particles are placed on an acoustic transducer and their separation is measured as a function of frequency and amplitude of the vibrator.

A microbalance was used by Corn (1961) to measure directly the adhesional forces between a flat glass surface and simulated test particles created from heated fibres of quartz or Pyrex glass. The effect of time of contact on adhesion was studied and the author concluded that when using surfaces which have been exposed to high humidities, short contact times of five minutes duration yielded average values of adhesional force comparable to those obtained with contact times measured in hours. Another observation from his experiments also showed that there was little difference in the adhesional force of small particles as compared to larger ones. The author suggests that small particles retain moisture adsorbed at the contact interface and do not adapt as rapidly as large particles to changing ambient conditions. A microbalance was also used in measurements of the adhesional energy by Abdel-Ghani et al. (1991). In order to determine the adhesional energy, the force necessary to separate two smooth glass surfaces, one spherical and the other planar, was measured directly. The measurements were performed by bringing a 5 mm radius spherical lens and a glass microscope slide into contact using a micro-motion stage and determining the adhesional force at a separation velocity of 10 μm s⁻¹. Adhesion was not detected in the uncleaned state. However, when the lens and slide were cleaned in acetone, an adhesional force was obtained and this increased with humidity by a ‘relatively small but significant extent’. The authors suggest that adhesion results from a capillary bridge or adsorbed layer formation but values of relative humidity of the surrounding air and adhesion forces at these humidities are not given.

Gillespie and Settineri (1967) adapted an interfacial tensometer from its normal function of measuring surface tension, to measure directly the adhesional forces between two spheres. The authors studied the adhesional forces in liquid bridges formed from water and mineral oil. They found that larger bridge volumes yielded smaller adhesional forces in accordance with classical capillary force theory. The reverse dependence was found by Mason and Clark (1965) and later by Mazzone et
al. (1986). This disagreement may be due to a number of factors. In Gillespie and Settineri's (1967) experiments, the effect of separation on the adhesion force was not investigated. Mason and Clark (1965) and Mazzone et al. (1986) have both demonstrated that the maximum adhesion forces occurred at very small separation distances of about 5% of the sphere radius after which the force decreases as the separation distance increases. The comparison between the experimental results to classical force expressions was also inadequate in the case of Gillespie and Settineri's (1967) investigation. The theoretical approaches used by these authors have neglected the buoyancy term, which can have significant influence over the measured force of the liquid bridge, (Wolfram and Pinter, 1979; Hotta et al., 1974).

Johnson et al. (1971) carried out experiments in which adhesional forces were measured for optically smooth particles, given by the negative load indicated by a balance at the moment when the contact was broken and surfaces separated from each other. The experiments were carried out to validate the proposed theory to describe the contact mechanics between two spheres. Using relatively large, soft rubber and gelatine spheres with diameters ranging from 4.4 cm to 5.0 cm contacted with rubber or Perspex flat surfaces, the authors showed that the adhesional forces for such intimate contact were as high as 0.4 N.

Harnby et al. (1996) have developed a technique to directly measure the adhesional force of single particles from an array of individual particles. The array is composed of several thousand particles placed in the apertures of an electroformed microsieve and 'frozen' in position within the apertures with an ultraviolet-curing adhesive. The adhesional force is measured with an electronic balance by firstly contacting the array and a surface, separating them, and then recording the greatest negative balance reading. In this way, the total adhesional force measured is the sum of several thousand individual contacts. The mean adhesion force for a single contact is then established by dividing the total adhesional force by the number of contacts in the array of particles. The authors propose that this mean value is more representative than an adhesional force based on a single, and possible atypical, contact point. However, the true number of contacts will be in reality a small fraction of the number of particles in the array. It is therefore not realistic to expect this method to yield force
data for single particles. From Hamby's *et al*'s work, the adhesion force of a 155 μm untreated glass ballotini particle interacting on a glass surface at 60% RH, deduced from the measurement of an array of particles published in this paper is 140 times less than the measured value of 7000 nN for a single glass ballotini particle interacting with a glass surface (Looi, L, 2001). The large discrepancy in these values can not be adequately explained by contamination, surface roughness or pretreatment of surfaces. It is felt to result from an overestimation of the number of contacts between the array of particles in Hamby *et al*.'s technique. Another disadvantage of the described experimental technique is the difficulty in constructing a stable array of particles.

### 2.3.2 Surface Force Apparatus (SFA)

The first device for measuring forces corresponding to molecular interactions as a function of distance between surfaces was developed by Tabor and Winterton (1969) and Israelachvili and Tabor (1972, 1973). The surface force apparatus (SFA) was used to measure van der Waals forces between molecularly smooth mica surfaces both in air and in vacuum. The sensitivity and flexibility of the original device was then refined by investigators such as Israelachvili and Adams (1976), Parker *et al*. (1989) and Stewart and Christenson (1990).

The force sensitivity of the SFA is about $10^{-8}$ N (Israelachvili, 1994). The SFA contains two curved molecularly smooth surfaces of mica (of radius ≈ 1 cm) between which the interaction forces are measured using a variety of (interchangeable) force-measuring springs. The two surfaces are in a crossed cylinder configuration. The separation between the two surfaces from microns down to molecular contact can be measured by use of an optical technique employing multiple beam interference fringes called Fringes of Equal Chromatic Order (FECO). From the positions and shapes of the coloured FECO fringes the distances between the two surfaces can be measured, usually to better than 0.1 nm, as can the exact shapes of the two surfaces and the refractive index of the liquid (material) between them; the latter allows for reasonably accurate determinations of the quantity of material deposited or adsorbed on the surfaces.
The force is measured by expanding or contracting the piezoelectric crystal by a known amount and then measuring optically how much the two surfaces have actually moved; any difference in the two values when multiplied by the stiffness of the force-measuring spring gives the force difference between the initial and final positions. In this way, both repulsive and attractive forces can be measured and a full force law can be obtained over any distance regime.

The SFA has been used extensively by various investigators to study a wide range of interaction phenomena, for example, Bailey et al. (1990) investigated the deformed shapes of adhering particles and vesicles, Chan and Horn (1985) and Israelachvili (1986, 1989) measured dynamic interactions and time-dependent effects, such as viscosity of liquids in very thin films and Helm et al. (1989) studied the fusion of lipid bilayers. The SFA however does not lend itself to work with fine particles, and hence is not suitable for the current work.

2.3.3 Atomic Force Microscope (AFM)

Imaging surfaces at high resolutions reached yet another milestone when Binnig et al. (1986) developed the Atomic Force Microscope (AFM). Its advantage over other types of instrumentation is its flexibility. The AFM can be used to acquire high resolution topographical information on a surface which can typically be as large as 100 $\mu\text{m}^2$, or measuring force interactions between the tip and the sample in liquid, in air or in vacuum, with little or no sample preparation.

The AFM operates by scanning a sharp probe tip located at the end of a cantilever spring over a sample surface. Deflections of the spring can therefore be translated into a relief map of the surface. The scanning movement is achieved by applying controlled voltages to piezo ceramic transducers. The cantilever deflection is measured by reflecting a laser beam off the back of the cantilever, and by monitoring the reflected spot on a photodiode detector. The resulting force versus separation curve can then be acquired to provide information on the adhesive, attractive or repulsive forces acting between the tip and the sample. A typical force curve is shown in Figure 2.2 and the analysis of the curve is as follows:
Region A At large separations the cantilever remains stationary. The cantilever, placed at the end of an expanding piezo ceramic is brought closer to the sample surface.

Region B When the surface is typically within a few tens of nanometers from the cantilever, the two surfaces experience a mutual interaction resulting in a deflection of the spring. This interaction can be attractive or repulsive. If the force is attractive, then a point of mechanical instability is often observed and the spring snaps into contact with the sample surface.

Region C Further sample motion in the same direction bends the cantilever backwards and increases the loading force of the cantilever tip against the surface.

Region D When the piezoelectric ceramic is contracted and the contact load is reduced, the cantilever tip adheres to the surface causing the cantilever to bend down.

Region E The cantilever tip continues to adhere until the bent cantilever generates enough force to pull the tip off the surface. The cantilever then returns to its resting position.

Figure 2.2 Typical force curve and its tip movement

The cantilever spring is typically 0.6 to 2 μm thick and, depending on the geometry and length can have a wide range of force constants. The displacement of the
cantilever is detected optically with a precision of about 0.1 nm. This corresponds to a maximum force sensitivity of 0.003 nN for a spring constant of 0.03 N/m.

From an unloading curve, one can obtain the removal force of the cantilever tip from the surface. The removal force is proportional to the maximum downward displacement of the cantilever. The constant of proportionality or the spring constant, \( k \), of the cantilever can be calculated from the geometry of the cantilever and the elastic modulus of silicon nitride. Other methods for determining the spring constant are presented and discussed in Section 2.4.1.

Many modes of operation have now been developed for a commercial AFM, the four basic modes of operation being

1. Constant force mode normally favoured for mapping and scanning sample topography.
2. Constant height mode used for detecting surface forces at different regions of the sample.
3. Vibrational modes, also known as intermittent contact or tapping mode (Zhong et al., 1993; Umemura et al., 1993). This mode is useful for imaging soft samples that would otherwise deform under the usual contact mode operation (Spatz et al., 1995; Chen et al., 1994).
4. Force-distance mode, normally used for measurements of surface forces.

Recent advances have increased the portfolio of AFM functions to include for example, magnetic mapping, frictional mapping, thermal imaging or chemical mapping of sample surfaces (Cappella and Dietler, 1999).

The individual components of the AFM will be discussed in greater detail in Section 3.5.
2.3.4 Comparison of the Atomic Force Microscope and Surface Force Apparatus

Ducker et al. (1992) and Cappella and Dietler (1999) have extensively reviewed the advantages and disadvantages of the SFA and the AFM in terms of restrictions in operation and resolution and their observations and comments will be summarised below:

1. The primary difference between force measurements using the SFA and the AFM is the size of the substrates. In an AFM, micron sized particles may be mounted on a cantilever spring, hence the substrate radii are $10^4$ to $10^6$ times smaller than those used in the SFA.

2. The geometry of interacting surfaces can be either controlled or unspecified in an AFM whereas in the SFA, the cross-cylinder configuration is well-defined.

3. Until recently, the SFA was also restricted to measurements of forces between transparent substrates, but this limitation has been removed by the adoption of new force measuring techniques such as the piezoelectric-bimorph technology by Parker et al. (1989).

4. The AFM facilitates studies of topography and indentation, which are not available with a SFA.

5. Measurements may be performed at speeds $10^4$ greater in the AFM while maintaining the same viscous force to surface force ratio as in the SFA. This facilitates the measurement of fast phenomena such as relaxation effects, and more realistically reflecting collision speeds in many colloidal systems. Higher measuring speeds also minimize the effects of thermal or other drifts.

6. One of the major problems in surface force measurement is contamination of the surfaces with undesired adsorbed molecules. Since the probability of trapping contaminants in the zone between the substrates is proportional to the radius of the substrate the AFM is less subject to such contamination, and this has been borne out in experiments (Ducker et al., 1992).

7. Because the drift in the optical distance measuring technique utilised in the SFA is negligible, the SFA was much better suited for measurements in which a constant surface separation must be maintained. However, in the new generation of atomic
force microscopes, a strain gauge is attached to piezo scanners which minimises the drift.
2.4 ARTEFACTS IN AFM

While the AFM has many advantages over its predecessors in terms of resolution and wide range of operation modes, many aspects of the technique and interpretation of results are still being investigated. In the subsequent sections, the following artefacts associated with AFM will be addressed:

- Spring constant determination
- Working with particles
- Particle mounting
- Cantilever and probe tip geometry
- Mechanical stability
- Hysteresis
- Noise
- Surface roughness

2.4.1 Spring Constant Determination

One major criticism of the use of an AFM for force measurement is the uncertainty in the absolute magnitude of forces, which arises from uncertainty in the cantilever spring constant. Springs are usually assigned a nominal spring constant by the manufacturers. These values can vary by ±30-40% from the true value. A number of different approaches have been used to quantify the true values of the spring constant. In this section, the various methods and equations previously used by investigators to determine spring constants are presented and discussed.

Classical Beam Theory

The following equation describes the spring constant for an end-loaded beam of rectangular cross section.

\[ k = \frac{Ew}{4\left(\frac{t}{l}\right)^3} \]  

Eqn. (2.7)
Here \( w, t \) and \( l \) are the beam width, thickness and length respectively (Stokey, 1993). \( E \) is the Young’s modulus of the material. As the term \( tl \) scales to the power of 3, any small error in \( t \) or \( l \) can lead to a significant error when calculating the spring constant. It has been shown that a V-shaped cantilever can be approximated by two rectangular beam cantilevers, Cleaveland et al. (1993) and Albrecht et al. (1990). Hence, for V-shaped cantilevers, the spring constant of a V-shaped cantilever may be estimated by the following equation:

\[
k = \frac{Ew}{2} \left( \frac{t}{l} \right)^3
\]

\( Eqn. (2.8) \)

Cleaveland et al. (1993) have observed variations in cantilever thickness ranging from 0.4 to 0.7 \( \mu \)m. Sendon and Ducker (1994) stated that the anisotropic growth of the \( \text{Si}_3\text{N}_4 \) film could lead to variation in Young’s modulus. This is discussed further by Weissenhorn et al. (1992) who commented that when using low pressure chemical vapour deposition (LPCVD) techniques, the stoichiometry of the silicon nitride film can range significantly from \( \text{Si}_3\text{N}_4 \) to \( \text{Si}_3\text{N}_4 \). Dey (1998) has highlighted the vast difference in published values of Young’s modulus of silicon nitride (see Table 2.2).

<table>
<thead>
<tr>
<th>Source</th>
<th>( E \times 10^{11} ) N/m(^2)</th>
<th>Application</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sarid &amp; Elings (1991)</td>
<td>1.5</td>
<td>AFM</td>
</tr>
<tr>
<td>Senden &amp; Ducker (1994)</td>
<td>3.0</td>
<td>AFM</td>
</tr>
<tr>
<td>Kawai et al. (1992)</td>
<td>2.94</td>
<td>AFM</td>
</tr>
<tr>
<td>Hutter &amp; Bechhoefer (1994)</td>
<td>1.5</td>
<td>AFM “typical value” for ( \text{Si}_3\text{N}_4 )</td>
</tr>
<tr>
<td>Vlassak &amp; Nix (1992)</td>
<td>2.2</td>
<td>Non-AFM ( \text{Si}_3\text{N}_4 ) film</td>
</tr>
<tr>
<td>Lefevre et al. (1991)</td>
<td>3.5</td>
<td>Non-AFM ( \text{Si}_3\text{N}_4 ) thin window</td>
</tr>
<tr>
<td>Grow &amp; Levy (1994)</td>
<td>0.75-0.95</td>
<td>Non-AFM ( \text{Si}_3\text{N}_4 ) film at high temperatures</td>
</tr>
</tbody>
</table>

Given the dimensions, mass of cantilever and resonant frequency, Sader et al. (1995) calculated \( k \) based on far end point loading both under vacuum and in liquids. The effect of off-axis (from the centre line of the cantilever along its length) was also
investigated and found to be very negligible. On the other hand, the effect of a coating on the cantilever, for example, of gold was significant. A 10 nm coating of gold on a cantilever led to a decrease in the resonant frequency of a few percent. Although experimental results generally showed good agreement with Sader et al.'s theoretical treatment for the determination of spring constants, this technique is limited to the requirement for an accurate determination of cantilever mass for systems in vacuum and the precise knowledge of the Reynolds number for systems in liquid. Unless measurement of the cantilever mass could be performed during manufacture and supplied with the cantilever, and viscous effects could be eliminated in liquid systems, one is forced to determine the value via a calculation based upon the physical dimensions of the cantilever and density.

**Frequency Method**

Cleaveland et al. (1993) describe a method where $k$ is calculated from the shift in resonant frequency when an end mass is added to the cantilever, resulting in the following equation,

$$k = \left(2 \pi \right)^2 \frac{M_f}{\left(\frac{1}{\nu_f^2} - \frac{1}{\nu_0^2}\right)}$$

*Eqn. (2.9)*

Here $M_f$ is the added end mass, $\nu_0$ is the unloaded resonant frequency, $\nu_f$ is the loaded resonant frequency and $k$ is the spring constant. Measurements were made on 120 $\mu$m long, 22 $\mu$m wide V-shaped Si$_3$N$_4$ cantilevers ($k = 0.10 \pm 0.01$ N/m, $\nu_0 = 37 \pm 1$ kHz), 3 from the same wafer and 1 from a different wafer. Tungsten spheres (mean diameter 20 $\mu$m) were manipulated using micropipettes and mounted on the end of the cantilevers. The particle end mass was calculated by measuring the sphere radius and using the density for tungsten of 19300 kg.m$^-3$. Their technique was accurate to about 10%. The main source of error in this technique is due to the measurement of sphere diameter. Furthermore it requires very precise micromanipulating equipment to ensure that the added mass is positioned correctly. Sader et al. (1995) highlight the fact that this technique is sensitive to flaws or micro-cracks in the cantilever and so can be
used as a check for damage. No knowledge of beam dimensions or Young’s modulus is required, however no compensation is made for off end loading. Neumeister et al. (1994) showed the variation in normal spring constant as the location of loading moves back from the tip (0 - 9.5 μm). Sader et al. (1995) claim that true values of $k$ can be 30-60 % higher due to off end loading.

**Calibration Methods**

Butt et al. (1993) and Li and Lindsay (1991) describe static methods where a known force producing a measurable deflection is used to calibrate the cantilever spring. Butt et al. (1993) measured the spring constant directly by equating the deflection of a pendulum to the deflection of an AFM cantilever resting against it. The spring constant can be determined using the following equation:

$$k = \frac{M_p g \Delta z_p}{L \Delta z_c} \quad \text{Eqn. (2.10)}$$

where $M_p$ is the mass of the pendulum, $g$ is the acceleration due to gravity, $\Delta z_p$ is the displacement of the pendulum, $L$ is the pendulum length and $\Delta z_c$ is the cantilever displacement. The results are not entirely convincing with a quoted error of ± 50%. The source of the error was not explained in the paper.

Senden and Ducker (1994) modified Cleaveland et al's (1993) technique of measuring the static deflection of the cantilever when known masses are added to the end of the cantilever, by inverting the instrument to re-measure the deflection in the opposite direction. The spring constant is then given by

$$k = \frac{8 \pi R^3 \rho g}{3 \Omega x} \quad \text{Eqn. (2.11)}$$

where $R$ is the radius of the tungsten sphere used to load the cantilever, $\rho$ is the density of the tungsten sphere, $\Omega$ is the deflection calibration constant and $x$ is twice the displacement due to gravity. The total error to be expected from this method is quoted to be of 15%.
Thermal oscillations

Hutter and Bechhoefer (1993) determined their spring constants by oscillations of the cantilever caused by the energy due to thermal motion of the air molecules at temperature $T$, from the following equation:

$$\left\langle \frac{1}{2} m \omega_0^2 x_0^2 \right\rangle = \frac{1}{2} k_b T$$  \hspace{1cm} Eqn. (2.12)

for an effective mass of the cantilever $m$, resonant frequency $\omega_0$, amplitude $x_0$ and Boltzmann's constant $k_b$. Since $\omega_0^2 = \frac{k}{m}$ one obtains the following for $k$:

$$k = \frac{k_b T}{\left\langle x_0^2 \right\rangle}$$  \hspace{1cm} Eqn. (2.13)

The observed results were lower than quoted values from manufacturers by a factor of four. The difference between their calculated and measured values of spring constant was about 5%.

Walters et al. (1996) used the thermal method as well as a static loading method and both agreed within 20%, although his curves of spring constant versus cantilever length were plotted on a log-log scale thus averaging out any discrepancies that may be otherwise observed on a normal scale.

Summary of spring constant determination

It is clear that there have been many different attempts to obtain accurate and reliable information of spring constants. All of the techniques discussed above have their own merits and shortcomings in terms of reliability and reproducibility. The technique employed in this study relies on the Classical Beam Theory. The dimensions of the cantilever are crucial to the classical beam method, especially when evaluating the thickness of the cantilever, which is perhaps the most difficult parameter to assess. Scanning Electron Microscopy (SEM) is therefore used to accurately measure the...
dimensions of the cantilevers used in the adhesion studies to within 5% of error. The measured dimensions are then double-checked using an optical microscope capable of a resolution of 2 μm.

2.4.2 Working with Particles

One of the best ways to mount particles of any size on to a substrate involves suspending the particles in a non-dissolving liquid (for example, in de-ionized water or alcohol), depositing a drop of the suspension on a substrate and letting it dry in air or in an oven. Mica and graphite are good choices of substrate since cleaving can produce a clean surface. For larger particles, a thin film, such as gold, a bare sample puck, or a membrane filter may be useful as a substrate since the microroughness of the substrate can help anchor the particles in place (Zhdan, 1997).

Loose particles on a sample surface may cause image artefacts, particularly, when contact modes of scanning are used. These particles may stick to the AFM probe, causing streaking. They may also cause the image to appear to ‘jump’ as particles either adhere to or come off the tip. There are a number of different adhesives which are inviscid enough to spread into a sufficiently thin film for mounting particles. For each of these cases, it is important that the layer does not envelop the entire particle making the top surface of the particle inaccessible (Page, 1999).

During contact AFM imaging and force measurements, the probe can deform a soft sample. This can be seen by streaking of the sample image or by compression of the sample surface, resulting in inaccurate topographical results or in extreme cases, damage to the sample during force measurement (Zhdan, 1997).
2.4.3 Particle Mounting

The mounting of a single particle on to the back of a AFM spring cantilever facilitates the measurement of single particle interactions or interactions between a particle and a flat surface.

A technique for particle mounting has been previously described by Ducker (1996). An AFM cantilever is first attached to a micromanipulator, and a droplet of glue and a sample of particles are placed apart on the same glass slide. Viewing through an optical microscope, the tip of the cantilever is first dipped into the glue droplet, and then brought into contact with a chosen particle. Needless to say, this technique works best on a vibration-free surface.

The adhesive used to attach the particle varied amongst investigators. Tyrrell (1999) conducted an extensive review on this subject. Larson et al. (1993), Toikka (1996) and Braithwaite et al. (1996) all used Epikote (Shell Chemicals, UK), a high melting point epoxy, to fix particles to AFM cantilever springs. Epikote is first sprinkled on to a microscope slide, which is then placed on a heated stage. The Epikote melts and can be manipulated according to Ducker's technique. Removing the Epikote from the heat source allows it to solidify, fixing the particle to the cantilever. Adjustments can be made to the particle-cantilever system by returning it to the heat source and allowing the Epikote to melt.

UV active adhesives have also been used for particle mounting applications. The adhesive can be manipulated until it is exposed to UV radiation for 10-15 minutes at which point it hardens, fixing the particle to the cantilever. This method was favoured by Gady et al. (1998) and Schaefer et al. (1994).

Tyrrell and Cleaver (2001) adopted a technique using epoxy resin (Araldite) and a hydraulic micro-manipulation stage to fix a particle to the underside of an AFM

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1 OP60 adhesive, Dymax Corporation, Torrington, Connecticut, USA
spring. This method is employed in the current work. Details, including a diagram of the mounting fixture can be found in Section 4.4.

2.4.4 Cantilever and Probe Tip Geometry

Cantilevers and their tips are critical components of an atomic force microscope system because they determine the force applied to the sample and the ultimate resolution of the topographic image.

The geometry of the tip employed to measure forces or to image surfaces is important in order to evaluate the true contact area between the tip and the sample. A number of theoretical and experimental studies have assumed that these tips can be approximated as hemispheres of various radii ranging from a few nanometres to hundreds of nanometres. If the effective geometry of the AFM tip is hemispherical, then contributions to the total force of interaction (e.g., van der Waals, electrical double layer) as a function of surface separation may be quantitatively interpreted. This has been investigated by Drummond and Senden (1994). A series of scanning electron microscope (SEM) images of a microfabricated silicon nitride cantilever with an integrated tip was shown. A progression of magnifications showed that the tip was square-pyramidal in construction but has a rounded apex. The authors also demonstrated a method for determining the effective radii of microfabricated silicon tips. In the method, it was assumed that, for long-range interactions between tips and relatively flat surfaces in aqueous solutions, the tips are well approximated by spheres. The method utilises a defined standard sphere-flat plate interaction between two adsorbed surfactant bilayers to calibrate the interaction between silicon nitride tips and flat sample surfaces. The results showed that the range from 100 to 400 nm appeared to cover most values of effective radii. In this article, the effect of surface roughness was also discussed and the degree to which the roughness affects the force of interaction between two surfaces is thought to depend on several factors; the frequency and amplitude of roughness compared to the decay length of the surface force, the surface separation and the area of interaction.
The effect of tip radius on the measured adhesive force using an atomic force microscope was investigated by Sugawara et al. (1993). The authors used an ultrahigh vacuum (UHV) atomic force microscope to avoid meniscus forces with the objective of investigating the forces acting between the cantilever tip and a well-defined surface at small separation distances. The AFM used also incorporated a fibre-optic interferometer to detect the cantilever deflection. This method is based on the optical interference occurring in a micron-sized cavity between the cleaved end of the single-mode optical fibre and the cantilever. The samples used in the experiments were LiF crystals and mica sheets. The authors found that the adhesive force decreased before and after AFM imaging. This was attributed to organic contamination and/or a water film on the cantilever tip, which might be removed by the contact of the cantilever tip with the sample surface. In order to investigate the influence of the humidity and of the radius of curvature for the cantilever tip on the adhesive force, the tip-sample geometry was approximated by a perfect sphere on a perfect flat surface.

To investigate the effect of RH, Sugawara et al. used a mica surface and a microfabricated silicon nitride cantilever with a radius of curvature, $R$ of about 250 angstroms. The results showed that the adhesive force increases with increasing humidity, which agrees with the previous experimental results performed with a glass sphere of radius several millimetres (Bowden and Tabor, 1954), although it does not agree with the Laplace-Kelvin equations previously described in Section 2.2.3. The authors attributed this increase to the surface roughness of the probe tip, which will have multiple asperities.

### 2.4.5 Mechanical stability

When taking force measurements, the separation distance between the tip and the samples is gradually reduced, and the deflection of the cantilever as a result of attractive or repulsive forces is detected. However, in cases where the rate of change of attractive force with respect to separation between tip and sample exceeds the spring constant of the cantilever, the cantilever spring experiences a mechanical instability and jumps to a new equilibrium position. The problem of instability can occur on approach or separation of the surfaces. In the region of instability the force is
indeterminate. The distance over which the instability occurs could be reduced by using stiffer springs but then the sensitivity of the measurements is decreased. The distance over which the jump occurs on approach can be used to provide an estimate of the van der Waals attraction forces. An excellent exposition of this phenomenon is presented by Cappella and Dietler (1999). Care must be taken to distinguish a 'jump' to contact from adsorbed layer interaction or contact 'relaxation'. In the latter, the surfaces continue to move together with increasing contact area for some time after initial contact has been established.

2.4.6 Hysteresis

Hysteresis in force measurements may be categorized into three different types;
1. Force curve hysteresis due to mechanical instability of the cantilever
2. Irreversible interactions
3. Piezo hysteresis

Force curve hysteresis is the difference in path between approach and withdrawal curve (A→B→C in approach curve; C→D→E in withdrawal curve in Figure 2.2). If the spring constant of the cantilever is greater than the greatest value of the tip-sample force gradient, hysteresis disappears (Cappella and Dietler, 1999). On the other hand, if a stiff cantilever is used, the force resolution is decreased. Hence, a compromise must be reached.

Irreversible interactions in force curves can be observed in the loading and unloading region (Region C in Figure 2.2). If the two surfaces in contact are perfectly rigid and elastic, the loading and unloading curves will coincide. However, if the surfaces in contact are showing non-elastic behaviour, hysteresis will be observed in the solid-solid contact region. Burnham et al. (1993) discussed various reasons for this phenomenon and they are listed below:

- The effect of a succession of discontinuous increases in contact area on loading, followed by discontinuous decreases in area on unloading although not at exactly
the same load values. Evidence for such an effect has been published elsewhere (Ross et al., 1991). The "mini-jumps to contact" responsible for the discontinuities are thought to depend upon some form of nanometre-scale stepped topography.

- The effect of load upon any dipole layer or surface film that may be present; for example, this layer could be deformed by the load in such a way as to allow the separation to decrease. Any recovery on unloading could well be time-dependent. It could also allow the gaps in contact area between micro-protrusions to be partly filled in, again through deformation of surface film. Chen et al. (1991) found with a surface force apparatus the hysteresis to be enhanced by a number of factors:
  i. increasing the mobility of adsorbed surface layers
  ii. increasing the load and time that surfaces are in contact
  iii. increasing the rate of separation.

Hysteresis is also a characteristic exhibited by piezo ceramics. Hence, for accurate interpretation of AFM outputs, it is necessary that the piezoscanner is both well characterised in terms of hysteresis effects and designed for routine calibration. Basedow and Cocks (1980) find piezoceramic tubes to exhibit less hysteresis than discs. Fu (1995) states that a 15% variation in vertical sensitivity was revealed by a PZT (lead-zirconate-titanate) tube during vertical scans ranging from 0.4 to 2.5 μm. This could result in a high level of uncertainty when taking distance measurements from force curves. Hence, for precise and accurate measurements, a correction must be made to the data. Albrektsen et al. (1989) made no correction for piezo hysteresis when calibrating the sensitivity of their piezo-tube in the z direction, and simply drew a straight line through their calibration data. Several techniques are described in the literature (Tyrrell, 1999) for the height (z-axis) calibration of a piezo-ceramic sample translator, for example by Michelson interferometry (Aklbrektson et al., 1989), by using a linear variable differential transformer (LVDT) displacement transducer (Hutter and Bechhoefer, 1994), and by a capacitance method (Libioulle et al., 1991). All of these techniques are inconvenient, in that they require the piezo tube to be removed from the instrument and mounted on to the appropriate calibration device. Other techniques, by using a stepped pervskite crystal of SrTiO3 (Shieko et al., 1993), and by imaging monolayers of latex spheres spread on mica (Li and Lindsay, 1991) or
colloidal gold particles (Xu and Arnsdorf, 1994), are unsuitable for the present study as they require tube motion along the x and y axis. The most suitable technique is that of Jaschke and Butt (1994). Interference fringes detected on the position sensing diode and resulting from a difference in optical path length between incident laser radiation reflecting off the back of the cantilever, and off a small mirror placed on the sample stage, allow the calibration to be performed in situ. This technique will be described in greater detail in Section 3.4 in the following chapter.

2.4.7 Noise

Thermal fluctuations of the cantilever are a fundamental source of noise in atomic force microscopy. Butt and Jaschke (1995) calculated the resulting deflections for a cantilever with a free end and optical lever detector, to be of the order of 0.8 nm. However, their calculations were based on a bar-shaped cantilever of rectangular cross section. Many cantilevers, especially those of low spring constant (0.02 –2.2 Nm⁻¹) are ‘V’ shaped. Hutter and Bechhoefer (1994) suggested measuring the amplitude of the thermal noise as a technique for spring constant calibration. This method has been reviewed by Tyrrell (1999).

Alexander et al. (1989) constructed an AFM based upon an optical lever amplification technique. The apparatus was positioned on a concrete block suspended from the ceiling by elastic cords. A major source of noise was found to be deflections of the laser beam due to air turbulence, this was greatly reduced by enclosing the apparatus in an airtight chamber and waiting for approximately 30 minutes before beginning measurements.

Clark and Baldeschiwerler (1993) offer the following suggestions to help minimise mechanical noise within the instrument – (i) minimise the number of parts, (ii) keep structures small and mechanically stiff and (iii) make sure that vibrations induced by seismic and acoustic disturbances are common mode to the structure.
Chapter 2 Literature Review

Okano et al. (1987) mount their Scanning Tunneling Microscope (STM) upon stacked metal plates with Viton rubber pieces places among them to isolate the instrument from external vibrations. A similar technique is adopted by Sugawara et al. (1993).

Siedle and Butt (1995) provide experimental evidence to suggest that when a stepped discrete voltage ramp is used to drive the sample piezo, the cantilever oscillates after each step. The effect is demonstrated in the non-contact region where coupling occurs between the cantilever and the sample. It is significant when measurements are being made in a liquid and can be eliminated by ramping the sample piezo with a smooth, external signal.

Marti et al. (1992) investigated the bending that occurs as a result of the temperature gradient initiated by incident laser light on one side of the cantilever. They find that a 1mW laser diode with a power stability of 1%, gives a fluctuation of up to 1nm for gold-coated cantilevers in vacuum. However, under ambient conditions the bimetal effect is reduced due to the efficient cooling of the cantilever by air, and hence would not be considered a significant source of noise.

2.4.8 Surface Roughness

The influence of surface roughness of samples and probe tips on adhesion and interparticle forces has been observed and cited by many (Xie, 1997; Claesson et al., 1994; Massimilla and Donsi, 1976; Podczeck et al., 1995b; Burnham et al. 1990; Larson et al., 1993; Hebb et al., 1998; Drummond and Senden, 1994, Greenwood, 1996; Mizes, 1996).

Mizes (1996) measured the positional dependence of adhesion of a point probe to a variety of rough surfaces using an AFM. He hypothesized that for rough surfaces, particles that fit snugly into pits or grooves will feel stronger attraction to the surface, and particles that sit atop bumps or ridges will feel a weaker adhesion. Surface inhomogenities arising from the surface material or from adsorbates may cause particles to adhere more strongly to some regions over others. The particles also will vary in size and will have different charges and, therefore, each can feel a different
attraction to the same surface. Mizes (1996) used integrated pyramidal tips to probe the adhesion. The point of the tip has a radius of curvature less than 30 nm. Mizes recommended that the pyramid should have only one contact point with surfaces that are studied and should be homogenous over the area of the contact. The samples studied included polycarbonate surfaces and silicon surfaces. Adhesion maps were used by Mizes to quantify how surface roughness can change particle adhesion. Comparison of adhesion maps and topography maps shows directly that there is a strong topographic dependence of adhesion and that it dominates the adhesion for the surfaces studied.

Drummond and Senden (1994) examined the likely effects of surface roughness on the estimates of the effective radius of interaction between tip and sample. They stated that surface roughness can influence both measured electrical double layer and van der Waals interactions. There are two types of surface roughness considered by the authors; the random roughness of the solid inorganic (either silica or silicon nitride) surfaces and the surface roughness caused by the distribution of molecular surfactant protrusion in the surfactant systems. The authors described the rough surface interaction in terms of macroscopic reference planes in the individual surfaces that have a distribution of asperity heights. Using this method, they concluded that the surface roughness should not influence the estimation of the effective radius of tip-sample interaction. However, in general, the degree to which the roughness will affect the force of interaction between two surfaces will depend on several factors; the frequency and amplitude of the roughness compared with the decay length of the surface force, the surface separation, the area of interaction and the extent of water sorption.

Burnham et al. (1993) measured forces between Al$_2$O$_3$, graphite and mica and found that the forces are a factor of 10 lower than expected. The discrepancy was attributed to the presence of asperities or minitips with small radii of curvature on the surfaces. Xie (1997) studied FCC powder systems and showed that in the case of surface asperities being approximated to smaller particles, the interaction between two parent spheres (denoted as sphere 1 and sphere 2) decreases as the size of the smaller particle increases. This shows that the interaction between the smaller particle (attached to
sphere 1) and the parent particle (sphere 2) dominates the interaction of the sandwich contacting system when the smaller particle is larger than 0.1 μm. When two spheres come into contact, the diameter in the equations for calculating van der Waals forces should be replaced by the size of the surface asperities if the radii of these asperities are larger than 0.1μm. If the radii of the surface asperities are smaller than 0.01μm, the spheres could be treated as smooth.

Massimilla and Donsi (1976) characterised the effect of surface irregularities on Ludox catalysts by means of electron scanning microscopy even in the case of particles appearing as perfect microspheres under an optical microscope. Consideration of these irregularities reduces evaluated cohesive forces by about two orders of magnitude. The study also showed that:

(i) even accounting for surface irregularities, cohesive forces evaluated at each contact point between two particles are larger than gravity forces for the particles of 40 to 100 μm in diameter and particle specific gravity of 0.94 to 1.53;
(ii) due to the size distribution of irregularities, there is a wide spread in expected particle to particle forces;
(iii) the size distribution of irregularities is essentially independent of particle size for particle diameters between 40 to 150 μm.

The effect of surface roughness was also observed by Claesson et al. (1994). The adhesion force between water vapour plasma treated mica in air was much smaller compared to untreated mica. The measured values of interfacial tension against water appeared to increase after treatments despite the fact that the surface charge at neutral pH is lower. This was attributed to an increased surface roughness or the result of intruding hydroxyl-groups on the surface in place of the less polar Si-O-Si bonds present on untreated mica surfaces.
2.5 CONTACT MECHANICS

The adhesion and deformation of two bodies coming into contact with each other can be characterized in terms of contact mechanics. In the scope of the current work, contact mechanics models are used as a form of analysis to evaluate the contact area of the surfaces and to compare pull-off forces from direct force measurements.

2.5.1 Johnson-Kendall-Roberts theory (JKR)

Real particles are never completely rigid, and on coming in to contact, they deform elastically or plastically under the influence of an externally applied load as well as under the attractive inter-surface forces. The latter give rise to a finite contact area even under zero external load.

The contact between two smooth elastic bodies was first analysed by Hertz (1896) who related the contact area and surface deformation to elastic properties of the bodies. He calculated both the deformed profile and the stresses at the contact surface using the theory of continuum elasticity. However, Hertz theory does not take into account the surfaces forces which may be acting between the two bodies.

The first successful model for elastic contact, taking account of attractive surface forces was the JKR model, developed by Johnson et al. (1971). This is based on an equilibrium energy balance, and assumes that the attractive forces are confined within the area of contact and are zero outside. The resulting area of contact is reached when the total energy of the system, consisting of the stored elastic energy, the mechanical energy in the applied load and the lost surface energy, is a minimum. The theory states that the relationship between the contact radius, $a$, and applied load, $P$, for two elastic solids of radii of curvature $R_1$ and $R_2$, Young's moduli $E_1$ and $E_2$, and Poisson's ratios $\nu_1$ and $\nu_2$, is given by

$$a^2 = \frac{R}{K} \left[ P + 3\pi w A R + \sqrt{6w A RP + (3\pi w A R)^2} \right] \quad \text{Eqn. (2.14)}$$

where
\[ \frac{1}{R} = \frac{1}{R_1} + \frac{1}{R_2} \quad \text{Eqn. (2.15)} \]

\[ \frac{1}{K} = \frac{3}{4} \left[ \frac{(1-v_1^2)}{E_1} + \frac{(1-v_2^2)}{E_2} \right] \quad \text{Eqn. (2.16)} \]

and \( w_A \) is the thermodynamic work of adhesion which is related to the surface energies, \( \gamma_1 \) and \( \gamma_2 \), of the two dissimilar materials and their interfacial energy, \( \gamma_{12} \) by

\[ w_A = \gamma_1 + \gamma_2 - \gamma_{12} \quad \text{Eqn. (2.17)} \]

For two identical surfaces in contact, \( \gamma_1 = \gamma_2 = \gamma \) and \( \gamma_{12} \to 0 \) and Eqn. (2.17) reduces to:

\[ w_A = 2\gamma \quad \text{Eqn. (2.18)} \]

The model predicts that for a sphere of radius \( R \) contacting a flat surface, the load need to effect particle/substrate separation, \( P_s \), is given by:

\[ P_s = \frac{3}{2} w_A \pi R \quad \text{Eqn. (2.19)} \]

As the surfaces are pulled apart, the maximum force occurs when the area of contact is finite. At this point, the equilibrium becomes unstable and separation occurs. From Eqn. (2.19), it is evident that the JKR theory predicts the pull-off force to be independent of the modulus of the materials. Implicit within the JKR theory is the unrealistic assumption that the stresses become infinite at the edge of the contact area. This unphysical situation arises because the JKR theory is a continuum theory and implicitly assumes that the attractive forces between the two surfaces act over an infinitesimally small range (Israelachvili, 1992). This assumption may in some cases, underestimated loading due to high surfaces forces (Burnham and Kulik, 1999).
2.5.2 Derjaguin, Muller and Toporov theory (DMT)

An alternative approach for determining the relationship between adhesion and deformation of two surfaces in contact was proposed by Derjaguin et al. (1975) (hereafter referred to as the DMT model). The DMT theory treated the problem of particle adhesion from a molecular level and assumed that the shape of the adhesion-induced contact was Hertzian. As a direct consequence of this latter assumption, it was found that exactly half of the interactions occur within the contact region and the other half outside of the contact zone, unlike the JKR model which assumes that all interactions occur within the radius of contact. The DMT model shows that as the surfaces are pulled apart, the maximum force at separation occurs at point contact; the pull-off force being

$$P_s = -2w_A \pi R$$  \hspace{1cm} Eqn. (2.20)

As a result of the assumptions intrinsic in the JKR and DMT theories, the predictions by the two theories are radically different. Tabor (1977) showed that although both models predict the same power law dependencies of the contact radius on particle radius and Young's modulus, the contact radius predicted by the JKR model under no load conditions is approximately 1.8 times greater than that predicted by the DMT model. Moreover, the DMT model predicts that separation occurs when the contact radius, \(a\), vanishes. Finally the force predicted by the DMT model to effect separation is 4/3 as much as that predicted by the JKR model.

2.5.3 Muller Analysis

In an attempt to resolve the differences in the two approaches, a full analysis was carried out by Muller et al. (1980) using the equations of elasticity and assuming a Lennard-Jones potential for molecular attraction. Their analysis yielded a parameter \(\mu\), which determines the behaviour of the contact. The parameter \(\mu\) is defined as:
\[ \mu = \frac{32}{3\pi} \left[ \frac{2R w_i^2}{\pi E r^2 z_0^2} \right]^{1/3} \]  

Eqn. (2.21)

where

\[ \frac{1}{E^*} = \frac{(1-\nu_1^2)}{E_1} + \frac{(1-\nu_2^2)}{E_2} \]  

Eqn. (2.22)

\( E_1, E_2, \nu_1, \) and \( \nu_2 \) denote the Young's moduli and Poisson's ratios for material 1 and 2 respectively and \( z_0 \) is the interatomic spacing. The authors concluded for the case where \( \mu>1 \), (corresponding to larger particles, higher surface energies and lower Young's moduli), the JKR theory should approximately describe the adhesion of a particle to a substrate. On the other hand, if \( \mu<1 \), (corresponding to smaller particles, lower surface energies), and higher Young's moduli, the DMT model would be appropriate.

The discrepancies and applicability of the JKR and DMT theories have been thoroughly reviewed by authors such as Tabor (1977), Pashley (1984) and Muller (1983) and will not be further discussed here. For the scope of the current project, the main concern is to review the most suitable contact mechanics model in order to aptly describe the polymeric system under consideration. Following the analysis of Muller et al. (1980), it could be deduced that the JKR model is applicable to materials that are very adhesive, thus having large values of the work of adhesion and low values of elastic moduli, which applies to most polymer systems. Several groups of investigators have successfully demonstrated the suitability of the JKR model in describing the surface energies of the polymeric systems studied (Mangipudi et al., 1994, 1996; Chadhury and Whitesides, 1991; Chen et al., 1991 and Perutz et al., 1998).
2.5.4 Maugis-Pollock theory (MP)

It is possible that, even in the absence of an applied load, the surface-force generated stresses are sufficiently large to exceed the yield strength of one of the contacting surfaces. In this instance, plastic deformation will occur. This effect, originally postulated by Krupp (1967), was analysed theoretically by Maugis and Pollock (1984). According to their theory, when the deformation at the contact area is fully plastic, the load can be related to the contact radius by the following relationship:

\[ P + 2\pi \omega_A = 3\pi a^2 Y \]  
*Eqn. (2.23)*

where \( P \) is the externally applied load, \( \omega_A \) is the work of adhesion (as described in *Eqn. 2.17* and 2.18), \( a \) is the contact radius and \( Y \) is the yield strength of the yielding material and is related to the material's hardness by the approximation:

\[ H = 3Y \]  
*Eqn. (2.24)*

Under no external load, *Eqn. 2.23* reduces to

\[ a = \left( \frac{2\omega_A R}{3Y} \right)^{1/2} \]  
*Eqn. (2.25)*

In the absence of any external load, elastic and plastic adhesion-induced deformations at the contact area can be distinguished by the power law dependencies of the contact radius on the particle radius.

In the present work, evidence of plastic deformation at the interparticle contacts is apparent, (see Chapter 5), therefore *Eqn (2.23)* is used to evaluate the contact area of the contacting polystyrene surfaces under load. The stress, \((\text{Load/Area})\), associated with the applied load is then calculated to determine the yield point.
2.6 NANOINDENTATION

The use of nanoindentation for characterising the mechanical properties of materials at different relative humidities is a very powerful technique, enabling hardness and Young's modulus to be obtained as a function of penetration depth.

As a predecessor to nanoindentation, microindentation has been widely used in the pharmaceutical industry to characterise the mechanical properties of crystals (Duncan-Hewitt and Weatherly, 1989a and 1989b). In this technique, the surface of a specimen is probed, most commonly with a Vickers diamond, using minimum loads of 140 mN. The impression size, depth of indentation and the length of crack emanating from the diagonals of the impression are then measured with an optical microscope to determine hardness, Young's modulus and fracture toughness. A shortcoming of this technique is that samples having a size of a few millimetres are required for testing. Furthermore, the results are inferred from viewing the sample once the tests are complete. Dynamic information such as strain rate effects and creep is not obtainable.

More recently, nanoindentation, so called because of its high resolution in measuring displacements in the nanometre scale (Pollock, 1992), has been used successfully to measure the mechanical properties of small crystals (e.g. Arteaga et al., 1993). This technique has the capability for measuring hardness and Young's modulus using very small loads, making it suitable for performing very small indentations as low as 1 nm. It relies on producing a continuous recording of the load and displacement during a complete cycle of loading and unloading of an indenter (typically a Berkovitch diamond) into the surface. With special indenters, it is also possible to make indentations in brittle materials with radial cracks extending from the edges of the contact which allows the exploration of fracture behaviour at the micron scale and the measurements of fracture toughness in volumes of material a few microns or less in diameter.
2.6.1 Measurement of hardness and Young's modulus

Generally, in a nanoindentation test, after the specimen and the indenter are brought in contact, the load is increased at a prescribed rate until a desired maximum is reached, and decreased back to zero at the same rate. During this process, a continuous recording of the load and penetration depth, as shown as Figure 2.3, is produced. The hardness and Young's modulus can be inferred from this information using well-established methods (Doerner and Nix, 1986; Oliver and Pharr, 1992; Hainsworth and Page, 1994)

Figure 2.3. Typical nanoindentation curve acquired using a sharp conical tip on polystyrene tablet

From the nanoindentation curve shown in Figure 2.3, it is clear that upon initiation of unloading the load does not suddenly fall to zero, i.e. the unloading curve is not horizontal; instead the elastic component of the depth starts to recover so that contact between the material surface and the indenter is still maintained. The elastic
displacement continues to recover as the load is decreased, upon reaching zero load, the penetration depth reaches its final value, $h_f$. Several methods of analysis for interpreting the unloading curve have been proposed. An early successful method, of Doerner and Nix (1986), assumed that there was sufficient linearity in the initial stages of unloading so that the elastic behaviour could be approximated to the problem of an elastic contact under a flat punch, for which an analytical solution was known (Sneddon, 1965). More recently, Oliver and Pharr (1992) suggested that the flat punch approximation made by Doerner and Nix was not entirely adequate, and demonstrated this by performing indentations on several materials including quartz, aluminium and fused silica using a Berkovitch indenter. They found, in all cases, that the depth-load curves were not linear during unloading. In fact, they showed that the data were better described by power law relations. For the materials studied, Oliver and Pharr (1992) found experimentally that the power law exponents varied from 1.25 to 1.51, and concluded that these values were distinctly greater than one, suggesting that the data were not consistent with the flat punch behaviour.

One method which has also been developed recently is that of Hainsworth and Page (1994). For many stiff materials and inhomogeneous systems (e.g. those employing thin hard coatings), they have shown that the test volume displays considerable elastic recovery as the load is removed so that the unloading curve does not fit particularly well any of the two models described previously. In the model of Hainsworth and Page, either the Young's modulus or hardness is required to be known a priori, and the depth-load curve during loading is then analysed to calculate the other mechanical property. This offers a tractable alternative in those cases where analysis of the unloading curve is unfeasible.

For the present work, the relationship between the penetration depth and the load fitted very well a power law function; therefore, the method of Oliver and Pharr (1992) was used to analyse the data. A description of this method is given below.
2.6.2 Hardness determination

The parameters used in the method of Oliver and Pharr (1992) are defined in Figure 2.4 which shows a schematic representation of the cross-section of an indentation.

According to this model and as proposed by Loubet et al. (1984), the total displacement, \( h \), at any time during loading, can be written as

\[
h = h_c + h_s
\]

\text{Eqn. (2.26)}

where \( h_c \) is the contact depth, \( i.e \) the depth along which contact is made, corresponding to the contact size, \( a \), and \( h_s \) is the elastic displacement of the surface at the perimeter of the contact. The unloading curve is then fitted with a power law relation of the form;
where $P$ is the indentation load, $h$ is the displacement, $B$ and $m$ are empirically determined depending on material fitting parameters ($m = 1$ for flat punch, $m = 1.5$ for paraboloids and $m = 2$ for conical geometries), and $h_f$ is the final displacement after complete unloading. The unloading stiffness is then established by differentiating Eqn. (2.27) at the maximum depth of penetration, $h = h_{\text{max}}$, i.e.,

$$S = \left( \frac{dP}{dh} \right)_{h = h_{\text{max}}} = mB(h_{\text{max}} - h_f)^{m-1} \quad \text{Eqn. (2.28)}$$

The contact depth is estimated from the load-displacement data using:

$$h_c = h_{\text{max}} - \varepsilon \left( \frac{P_{\text{max}}}{S} \right) \quad \text{Eqn. (2.29)}$$

where $P_{\text{max}}$ is the peak indentation load and $\varepsilon$ is a constant which depends on the indenter geometry. Empirical studies have shown that $\varepsilon = 0.75$ for a Berkovitch indenter and $\varepsilon = 0.72$ for a conical geometry.

The projected contact area of the hardness impression (assumed to be the contact area), $A$, is estimated by evaluating an empirically determined indenter shape function at the contact depth, $h_c$; that is

$$A = f(h_c) \quad \text{Eqn. (2.30)}$$

The shape function relates the cross-sectional area of the indenter to the distance from its tip. The functional form of $h_c$ must be established experimentally prior to analysis. The method is based on the notion that, at peak load, the material conforms to the
shape of the indenter to a certain depth; if this depth can be established from the load-displacement data, the projected area of contact can be estimated directly from the shape function. For a conical shaped indenter, the shape function can be estimated by the following method.

Figure 2.5 Schematic for the determination of the shape function of a conical tip

\[
\tan \theta = \frac{r}{h_c} \quad \text{Eqn. (2.31)}
\]
\[
r = \tan \theta h_c \quad \text{Eqn. (2.32)}
\]
\[
A = \pi r^2 \quad \text{Eqn. (2.33)}
\]

where \( \theta \) is the half-angle of the conical tip, \( h_c \) is the contact depth and \( A \) is the projected area of contact.

Once the contact area is determined, the hardness can be calculated from

\[
H = \frac{P_{\text{max}}}{A} \quad \text{Eqn. (2.34)}
\]

where \( A \) is evaluated from Eqn. (2.31) to (2.33)
2.6.3 Young's modulus determination

For measurement of Young's modulus, the unloading portion of the depth-load data can be analysed according to Sneddon's relation (Sneddon, 1965):

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

Eqn. (2.35)

where \( S \) is calculated from Eqn. (2.28); \( A \) is given in Eqn. (2.31) to (2.33) and \( E_r \) is the reduced modulus (Stilwell and Tabor, 1961) which is defined as

\[ \frac{1}{E_r} = \frac{(1-\nu^2)}{E} + \frac{(1-\nu_i^2)}{E_i} \]  

Eqn. (2.36)

where \( E \) and \( \nu \) are the Young's modulus and Poisson's ratio of the specimen, and \( E_i \) and \( \nu_i \) are the corresponding parameters for the indenter. Eqn. (2.35) has been found to be independent of indenter geometry (Pharr et al., 1992) and is therefore applicable to results obtained with a conical indenter.

2.6.4 Pile-up influences on hardness and Young's modulus measurement

The influence of pile-up and the conditions at which the Oliver-Pharr analysis are invalid have been examined in detail by Bolshakov et al. (1996, 1998) using finite element analysis. The authors proposed a simple measurable parameter which can be used to identify expected indentation behaviour of a given material. The proposed parameter is the ratio of final indentation depth, \( h_f \) (the depth of the hardness impression after unloading) to the depth of the indentation at peak load, \( h_{\text{max}} \). These two depths can be easily extracted from the unloading curve in a nanoindentation experiment. The natural limits for the ratio of \( h_f / h_{\text{max}} \) are between 0 and 1, whereby
the lower limit corresponds to fully elastic deformation of the material and the upper limit denotes rigid-plastic behaviour.

According to the authors, the amount of pile-up or sink-in is dependent on the amount of work-hardening of the material and is related to the ratio of $h_f / h_{max}$. Specifically, the amount of pile-up is large only when $h_f / h_{max}$ is close to the value of 1 and the amount of work-hardening is small. When $h_f / h_{max}$ was less than 0.7, very little pile-up is found no matter what the work-hardening behaviour of the material is. From the results of finite element analysis, it was evident that the Oliver-Pharr method can significantly underestimate the true contact area for materials in which pile-up is important. Furthermore, when $h_f / h_{max}$ was larger than 0.7, the accuracy of the Oliver-Pharr method depends on the amount of work-hardening in the material. It was shown that if the material is elastic-perfectly plastic, the Oliver-Pharr method underestimated the contact area by as much as 50%. On the other hand, contact areas for materials which work-harden during indentation are in excellent agreement with the analysis.

In a recent paper by Pharr (1998), the author remarked upon the effect of pile-up on the estimation of the effective Young's modulus. According to him, when pile-up is significant, the effective Young's modulus may be largely overestimated. Also, even when the amount of pile-up is small, that is, in material with high yield stresses and/or high work-hardening (characterised by the ratio of $h_f$ and $h_{max}$), the Oliver-Pharr method overestimates the effective modulus by 2-9% caused by lateral displacements of the indenter at the contact interface. When $h_f / h_{max}$ is larger than 0.7, the effective modulus is overestimated by 10-16%, presumably by the inadequacy of elastic solutions intrinsic in the Oliver-Pharr method in describing plastic behaviour in materials.

In the nanoindentation studies carried out in the current work, the Oliver and Pharr (1992) analysis is used to evaluate the hardness and effective Young's modulus of cross-linked polystyrene at low RH and high RH. The effect of pile-up is established by evaluating the $h_f / h_{max}$ ratios, obtained directly from the load versus displacement curves.
2.7 INTERACTIONS WITH POLYSTYRENE

Polystyrene is regarded as a common polymer with many applications in industry. However, there did not appear to be a significant amount of fundamental research dedicated to this material and hence, the behaviour of polystyrene is not a clearly understood science. There have been experimental studies investigating the effect of applied load and contact time of a single polystyrene particle interacting with a variety of substrates in ambient conditions. These studies will be described and discussed in this section.

The behaviour of polystyrene particles when in contact with another surface has been studied extensively by Rimai and co-workers (1990, 1993, 1994, 2000). In particular, the investigators were interested in the deformation and creep behaviour of cross-linked polystyrene particles as a result of adhesion-induced stresses. In all their investigations, the contact radii of a single cross-linked polystyrene particle placed on a substrate have been measured by Scanning Electron Microscopy (SEM). Their results revealed a non-linear relationship between the particle radius and the contact radius, in conflict with the linear relationship proposed by the Johnson-Kendall-Roberts (JKR) model. When comparing their results with the Maugis-Pollock (MP) model which takes into account plastic deformation at contact zones, the agreement was much better. This suggests adhesion-induced plastic deformation to be occurring on the polystyrene samples.

Another interesting observation by the authors was the time dependence of the apparent interparticle bridging by the substrate. This behaviour is reminiscent of creep, and together with the observation of craters after the particles were removed, further illustrates that the stresses generated by the surface forces are sufficient to cause certain materials to deform plastically. Such phenomena have previously been reported by DeMejo et al. (1992) who found unexpectedly large menisci, interparticle bridging by the substrate polymer and severe encapsulation for a variety of particles on an alternating block polyester-polydimethylsiloxane (PDMS) copolymer. Similarly, Vrtis et al (1994) reported that upon removal of tin and gold particles by amalgamation with mercury from the substrate material, evidence of craters and
accompanying menisci suggest that the forces of adhesion may be inducing creep of the substrate polymer in contact with the particles.

Schaefer et al. (1994) have used an AFM to study the interactions of 5-7 μm cross-linked polystyrene particles on silicon substrates. Unlike the SFA, the contact geometry and area could not be estimated by AFM. Hence, the authors have integrated their force-distance data to evaluate the values of surface energy of polystyrene. The obtained values were lower by a magnitude of 10 in comparison to values previously reported by Rimai et al. (1990). The discrepancies were attributed to plastic deformation of the polystyrene samples caused by adhesion forces (Rimai et al., 1993), shorter contact times which may lead to poor establishment of thermodynamic equilibrium between the particle and substrate, and the presence of microasperities between the particle and substrate in the contact zone.

In the same paper, Schaefer et al. (1994) also measured the pull-off forces of a 5 μm diameter polystyrene sphere in contact with a silicon surface at increasing applied loads under ambient conditions. The results show a slight increase in pull-off forces with the maximum loading force. However, it should be noted that the loading force in their experiments was no greater than 52 nN which compared to our present study, is very small. If the system studied was governed by elastic behaviour, the pull-off forces should be independent of the loading force due to elastic rebound of the materials. It was therefore likely that the observed non-linearity was due to either viscoelastic or inelastic responses of the particle to the load. By analysing the loading and unloading regions of the acquired force curves and comparing the contact regions of the curves with an infinitely hard system, the deformation of the polystyrene particle under a 50 nN load was calculated to be as high as 50 nm.

In a more recent paper by Reitsma et al. (2000), the effect of applied load on the force of adhesion between a single polystyrene particle and flat silica has been investigated. The polystyrene particle was subjected to an increasing applied load of 3.5 μN to 95 μN and there was a clear increase of the pull-off forces measured. When the same particle was subjected to another run of increasing applied load, the trend of increasing pull-off forces was observed again. In the second run, the pull-off forces
were consistently higher compared to the first run. This shows that non-elastic deformation is occurring at the contact area of the surfaces and the deformation is not reversible by a decrease in load. The non-elastic effects were further confirmed when adhesion forces were measured increased with increasing contact time. This is clear evidence of time-dependency on the pull-off forces, reminiscent of visco-elastic behaviour. However, the applied load at which the time-dependency experiment was conducted was not stated in the paper. When the authors examined the polystyrene particle after the experiments using electron microscopy, flattened regions on the particle were observed, reinforcing the hypothesis of plastic deformation of the particle.

One of the very few studies of the adhesion forces between two polystyrene surfaces was carried out by Schmitt et al. (1999). Experimental studies were conducted using a polystyrene droplet with a radius of 1 mm interacting on another polystyrene droplet. It was observed that the magnitude of pull-off forces decreased with increasing number of measurements at a constant applied load. The authors attributed this phenomenon to the cohesive failure within one (or both) of the surfaces which roughens the surfaces (e.g. by the creation of small polystyrene flakes) although no topographical images of the surfaces after force measurements were given as evidence of this. In some cases, the pull-off forces measured were higher than the predicted values by JKR. The magnitude of the difference could not be evaluated as no experimental data above the predicted values were presented in their paper. However, the authors explained the high pull-off forces by an increase in contact area of the two spheres caused by the detachments of small flakes of polystyrene from the bulk polymer on separation of the two surfaces. Pull-off forces between the polystyrene surfaces were also measured at ambient conditions with increasing applied load. The results showed an increment in adhesion forces\(^2\) of 50 mN/m as the applied load was increased from 14 mN/m to 33 mN/m. This was attributed to the flattening and plastic deformation of asperities protruding from the surfaces.

\(^2\) adhesion forces was scaled by dividing by the particle radius to enable comparison of results from different sized particles
From published literature, the behaviour of contacting polystyrene surfaces may not be adequately described by established elastic contact mechanics theories. The experimental evidence seemed to suggest non-elastic deformation behaviour.
CHAPTER 3  FORCE MEASURING INSTRUMENTS
FOR ADHESION STUDIES

3.1 INTRODUCTION

Surface interactions between a single polystyrene particle and a polystyrene substrate were measured using two instruments; a custom-built force measuring instrument based on the concept of an Atomic Force Microscope (AFM), and a commercial AFM Explorer. The initiation and construction of the custom-built instrument is described in detail by Tyrrell and Cleaver (2001). In this chapter, the main operating principle of the custom-built instrument will be described. The main features of the AFM Explorer used in this project will also be discussed.

3.2 CUSTOM-BUILT FORCE INSTRUMENT LAYOUT

The instrument, as shown in Figure 3.1, is housed in an enclosed chamber to facilitate varying the relative humidity of air. The chamber also serves to isolate the instrument from the influence of air drafts. The instrument is placed on an anti-vibration table to minimise vibrational noise from the surroundings.
The instrument features a minimum of components to ensure a rigid construction. All the parts of the instrument are easily adapted and repositioned for adjustments and modifications, necessary for purposes of piezo calibration for example. The open architecture also allows for manual inspection of the reflected spot of the cantilever on the photo sensor diode to ensure precise alignment of the laser spot on the back of the cantilever.

The layout of the instrument is detailed below:
Figure 3.2 Side elevation of the force instrument (Tyrrell and Cleaver, 2001)

1. support beam mount
2. pillar
3. laser (dashed line represents beam path)
4. support beam for AFM cantilever
5. piezo (see detail)
6. motor driven vertical sample translator
7. position sensing detector
8. single-axis manual translator
9. motor driven single-axis translator

Figure 3.3 Detail of piezo assembly (Tyrrell and Cleaver, 2001)

1. support beam for AFM cantilever
2. mounting plate for microfabricated cantilever
3. microfabricated AFM cantilever
4. sample
5. stainless steel sample mount
6. magnet
7. Tufnol disc
8. grounded copper disc
9. piezo tube
3.3 PRINCIPLE OF OPERATION

The principle of operation of the instrument is very similar to that of the Atomic Force Microscope previously described in Section 2.3.3 when operating in point-spectroscopy (force-distance) mode. A flat sample is mounted at the end of the piezo tube. A small particle is attached to the end of a microfabricated AFM cantilever spring. The laser beam is focussed on to the back of the cantilever tip and reflected on to the position sensing detector (PSD). This configuration is known as the 'optical lever', which enables the detection of very small deflections of the cantilever tip.

The flat sample is moved mechanically to within a few microns of the particle on the cantilever tip. A voltage signal is applied across the piezo tube which causes it to advance and contract by approximately 4 microns. The exact relationship between piezo displacement and voltage is determined during the piezo calibration procedure, (see Section 3.4). When the two surfaces, i.e., the particle attached to the cantilever tip and the flat sample mounted on top of the piezo tube, are in close proximity, typically within a few tens of nanometers from the particle, they experience a mutual interaction resulting in a deflection of the spring. This interaction can be attractive or repulsive, depending on the specific characteristics of the surfaces and the intervening medium. If the force is attractive, then a point of mechanical instability is often observed and the spring snaps into contact with the sample surface. Further sample motion in the same direction bends the cantilever backwards and increases the loading force of the particle against the surface. When the piezoelectric ceramic is contracted and the contact load is reduced, the particle adheres to the surface causing the cantilever to bend down. The particle continues to adhere until the force associated with the deflection is sufficient to pull the particle off the surface. This is commonly known as the 'pull-off' force or the force of adhesion. The cantilever then returns to its resting position.

The magnitude of the force experienced by the particle on the cantilever is given by Hooke's law

\[ F = kx \]

Eqn.(3.1)
where \( k \) is the spring constant of the cantilever and \( x \) is the deflection of the cantilever measured in distance.

The interaction between the surfaces can be represented by a plot of the force acting on the cantilever as a function of vertical movement of the sample on the piezo stage. A schematic of a typical force curve and the corresponding interaction are shown in Figure 2.2 in the previous chapter.

### 3.4 PIEZO CALIBRATION TECHNIQUE FOR THE CUSTOM-BUILT INSTRUMENT

The piezo displacement was calibrated using the technique suggested by Jaschke and Butt (1995), with a polynomial model (Libioulle et al., 1991) fitted to the data (Tyrell and Cleaver, 2001). The calibration technique exploits interference effects between coherent laser radiation reflected off the back of the cantilever and from the sample surface. Such effects, observed as modulations in the PSD signal, are sometimes seen when imaging a reflective sample surface using a commercial AFM (Attard, 1999).

The procedure adapted for the calibration of the force instrument is detailed in Appendix 1.

#### 3.4.1 Piezo calibration results

The piezo displacement-voltage relationship was characterized using a second order polynomial expression, derived by Libioulle et al. (1991) to account for both the linear expansion of the piezo and the hysteresis between expansion and contraction cycles (Tyrell and Cleaver, 2001)

The piezo model is described by Equations (3.2) and (3.3) below;
Expansion component

\[ S = aV^2 + bV \] \hspace{1cm} \text{Eqn (3.2)}

Contraction component

\[ S = aV_m^2 - a(V - V_m)^2 + bV \] \hspace{1cm} \text{Eqn (3.3)}

where, \( S \) is the piezo displacement, \( a \) and \( b \) are model constants, \( V \) is the applied potential and \( V_m \) is the maximum applied potential. Parameter \( a \) compensates for hysteresis effects and parameter \( b \) is a linear expansion coefficient.

The piezo model is incorporated into the data processing software, HPVEE, written specifically for the custom-built instrument converting a voltage applied across the sample piezo into its corresponding displacement value. The gradient of the voltage supply to the piezo determines whether the piezo is expanding or contracting and consequently identifies which component of the piezo model should be used for hysteresis correction.

Figure 3.4 Example of a piezo calibration curve
Calibration data are placed into a spreadsheet and correlated against the piezo model by adjusting the value of parameters $a$ and $b$. Appropriate values, shown below in Table 3.1, are identified using a least squares technique, i.e. values of parameters $a$ and $b$ are selected so that the difference squared between experimental data and calculated displacement is minimized.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A$</td>
<td>0.004 nm$\cdot$V$^{-2}$</td>
</tr>
<tr>
<td>$B$</td>
<td>5.0 nm$\cdot$V$^{-1}$</td>
</tr>
<tr>
<td>$V_m$</td>
<td>496 V</td>
</tr>
</tbody>
</table>

Parameter $a$, providing hysteresis compensation, is system specific. The linear piezo response is described by parameter $b$. Both values obtained from the calibration procedure agrees well with values previously obtained by Tyrrell (1999) using the same type of ceramic piezo and with previously published results by Albrightson $et$ $al$. (1989) and Libioulle $et$ $al$. (1991).

### 3.4.2 Effect of piezo hysteresis correction on acquired force curves

The effect of piezo hysteresis is appropriately corrected when the approach and withdrawal force curves for rigid surfaces are coincidental at the contact region. Hence, to test the values of parameters $a$ and $b$, obtained in the previous section a bare silicon nitride probe tip was brought into contact with a silicon wafer surface. The resulting force curve (Figure 3.6) shows coincidence of approach and withdrawal curves, confirming the values of $a$ and $b$ from Table 3.1 are correct.
Figure 3.5 Piezo displacement versus detector voltage curve without hysteresis correction for a silicon nitride probe tip on silicon wafer

Figure 3.6 Piezo displacement versus detector voltage curve with hysteresis correction for a silicon nitride probe tip on silicon wafer \((a=0.004 \text{ nmV}^2, b=5 \text{ nmV}^{-1})\)
Chapter 3 Force Measuring Instrument

3.5 THE ATOMIC FORCE MICROSCOPE EXPLORER (AFM Explorer)

The operating principle of the AFM Explorer has already been previously described in Section 2.3.2. In this section, the main operating components of the instrument will be described in fuller detail. The different modes of data acquisition used in the current project are described in the following chapter.

The AFM explorer consists of the SPM head which houses the piezo-electric ceramic on which the probe tip is mounted, a laser beam which reflects off a mirror and finally to the photodetector to detect the deflection of the probe tip, and a CCD camera which allows for the observation of the probe tip. A computer interface is then used to configure the microscope's data gathering parameters and to initiate a scan. A control module (ECU-Plus) contains the electronics which interfaces with the instruments for x, y and z position of the probe tip, data acquisition etc. Once the data are stored in the computer the image processing module of the SPM-Lab software is used to display and analyze the data.

3.5.1 Explorer Scanning Probe Microscopy (SPM) Head

The Explorer SPM head is the main part of the instrument. The head incorporates all the major components of the AFM. The assembly of the head is shown below in Figure 3.7.
3.5.2 Piezoelectric ceramic

The cylindrical piezoelectric ceramic used in the custom-built instrument is only capable of movement in the Z-direction whereas in the AFM Explorer, a tripod scanner is mounted in the SPM head. Tripod scanners are made from three distinct pieces of piezoelectric ceramic, mounted orthogonally. These create positive or negative scan motion in the x, y or z directions as voltage is applied to the appropriate piezo. As the x and/or y piezo are activated, they push against the base of the z piezo causing it to pivot laterally over a stationary pivot point. Applying voltage to the z piezo creates z movement. In the tripod scanner piezo configuration, the sample is mounted at the top of the z piezo. Because the x, y and z piezos are physically and electrically decoupled, the configuration creates less distortion in large-area scanning applications.

In all the experiments conducted in the present work using the AFM Explorer, the tripod scanner used is capable of 100 μm movement in the x and y direction and 10 μm movement in the z direction.
3.5.3 Feedback loop

An electronic feedback circuit uses the output of the probe/sensor to drive the z piezo-electric ceramic to create the z-positioning mechanism. A PID (proportional, integral and derivative) feedback control system is used. The feedback response is based on an equation that combines terms proportional to the error signal, the integral of the error signal and the derivative of the error signal to set the z position of the probe as to maintain a constant sensor signal. The error signal is the difference between the sensor signal and a user-defined set point. The optimum setting for the PID coefficients depends on sample properties, scan rate and the probe tip geometry. Therefore, they need to be determined experimentally.

When the interaction between the tip and sample increases, the output of the sensor increases. A differential amplifier compares the increased value from the sensor to the reference value and outputs a correction voltage. This drives the piezo-electric ceramic to pull the sensor away from the surface, restoring it to its original level. The feedback mechanism operates continuously to maintain constant tip/sample separation in non-contact imaging or to maintain constant force in contact mode imaging.

3.5.4 Beam alignment

Beam alignment is a vital step in all the operating modes in the AFM Explorer because it directly affects the quality of the information acquired. In beam alignment, three components must be adjusted, the laser, mirror and photodetector. When properly aligned, the laser beam bounces off the back side of the cantilever, to the adjustable mirror, then on to or near the centre of the quadrant photodetector. The objective of the alignment procedure is to maximise the signal generated by the beam at the photodetector, and to ensure that enough range is allowed on the detector for the measurement of current changes while the cantilever deflects during experiments.
3.5.5 Camera

Another additional feature afforded by the AFM Explorer which is absent in the custom-built instrument is the CCD video camera mounted on the SPM head. The CCD camera is equipped with a x50 lens from which observation of the tip movement when scanning or taking force measurements can be made.

3.5.6 Data processing software

The processing software used in the AFM is SPMLab version 5.01. The software operates in three modes: data acquisition, image analysis and screen editing. The functions of these three modes comprise all the data gathering, analysis and presentation software tools. These modes operate independently, using data originally obtained in the data acquisition mode.

3.5.6.1 Data acquisition mode

The data acquisition mode is where the instrument control and data acquisition parameters are set and the scan takes place. It is in this mode that the beam alignment is carried out. By adjusting the position of the laser, mirror and photodetector, the total sum signal on the 'detector signal' function on the data acquisition panel is then optimized. The 'tip approach' function is then activated to instruct the tip approach to the sample surface at a pre-set speed. Once the detector signal current reaches a predefined set-point, the computer will consider the system to be in feedback and activate the feedback loop to keep the sensor current at the set point. Once the system is in feedback, the PID settings can be adjusted to optimise the feedback loop. The scan size, scan rate and location of the scan on the surface can then be selected and the scan activated.
3.5.6.2 Image analysis mode

The image analysis mode can be sub-divided into three other modes: display, processing and analysis. In the display mode, functions such as background subtraction, contrast and brightness, 3D display and palette editing are controlled. Visualisation of the image is enhanced by these functions without affecting or distorting the original data. In the processing mode, image, curvature, leveling, convolutions, arithmetic processing, filtering etc. are handled. The main processing procedure used for the scans acquired in the present study is levelling. This operation is designed to remove curvature and/or tilt from an image. Because most modes of scanning probe microscopy describe the topography on a scale which is the absolute z height from some 'zero' point, the relative z value assigned to surface measurements is directly affected by how level the sample is. The levelling operation is carried out by using a least-squares algorithm to fit the image to a plane and then subtracting the plane from the image. Four different modes of leveling can be chosen to process the data; horizontal, which applies the levelling function from the top down, vertical, which applies the levelling function side-to-side, 2D levels the data in both x and y directions and 3 point, which allows the user to choose three points anywhere on the image which will designate the plane to which the image will be levelled. In the topography scans acquired in the present work, all the images are levelled using the 2D mode.

The analysis module of the SPMLab software is particularly useful for surface roughness measurements and indentation depth analysis as it allows the user to analyse the image with various statistical and measurement routines, such as line profile, peak and valley analysis and area analysis. The line measure function allows a cross-sectional measurement along a specified line, chosen from two individual points on the image. The x, y and z locations for the both points, the difference in x, y and z between the two points, the length of the line and the angle of the slope between the two points are then generated using the line measure function.

Peak and valley analysis is a measurement technique for analysing roughness by defining the lateral spacing and the angle (slope) of features. As opposed to other
analysis techniques that focus primarily on the z height component of the sample topography, peak and valley analysis allows roughness analysis based on peak density (lateral spacing) and on peak slope.

The function analyses peaks in the image along defined cross-sectional lines. Peak spacing is defined as the distances between neighbouring peaks. Peak angle is defined as the slope between a peak and its nearest valley. Separate histograms for peak angle and peak spacing are generated. The variables which may be altered in this function are line orientation, line interval, peak height, peak spacing and number of bins.

The line interval function allows definition of the number of lines that are used for analysis, for example, a setting of 10 would use every 10\textsuperscript{th} line for analysis. Peak height defines the minimum peak height that will be included in the analysis. Peak height is the distance from a peak to its nearest valley. All peaks greater than a pre-set height will be included. Peak spacing defines which features will be considered single peaks in the analysis. The value sets a minimum spacing allowable between two adjacent peaks before the software will determine the feature to be a single peak. Number of bins adjusts the number of histogram distributions bins for both peak spacing and peak angle. Assigning a large number of bins increases precision in the analysis.

The line analysis function allows the characteristics of user selected line profiles on the image to be measured. Once the line on the acquired image is selected, the line analysis report will generate the following information:

i) roughness average: the arithmetic average of the absolute values of the measured profile height deviations
ii) maximum height of the profile above the mean line
iii) maximum peak to valley height in profile
iv) mean values of roughness, more representative of the entire profile

Other forms of analysis such as height and fractal analysis can also be performed under this function.
3.5.6.3 Data presentation

Once the image has been processed and analysed, the data are then presented in the screen editor module. The module functions as a free-form presentation tool, allowing the manipulation and output of the gathered data. Text, lines, arrows, boxes and other graphic files can be added to the screen, and the position and size of the images, text and graphs can be modified. The final image can then be saved as any supported graphic file format (including TIF24, GIF and BMP8).
CHAPTER 4 EXPERIMENTAL TECHNIQUES

4.1 INTRODUCTION

This chapter details the experimental procedures performed for the investigation of interparticle forces and nanoindentation on polystyrene surfaces using the AFM Explorer. Sample preparation techniques of the polystyrene particles and the polystyrene substrate are also described.

4.2 MATERIALS

Cross-linked (1% DVB) polystyrene beads\textsuperscript{1} in the size range of 1-35 \textmu m in diameter are the primary samples chosen for the present study. In all experiments a ‘particle on flat’ configuration was studied with both contacting surfaces being of the same material. Due to the cross-linked property of the polystyrene beads, it proved impossible to obtain a flat surface by spin-coating or melting techniques. Hence, it was necessary to form a compacted tablet from the polystyrene particles in order to create a flat surface.

4.3 PREPARATION OF SURFACES

Polystyrene particles were mounted on to cantilevers without any prior preparation using the technique which will be described by Section 4.4. Compacted polystyrene tablets were formed from 2 grammes of polystyrene particles and compressed at high pressure, i.e., $1.08 \times 10^8$ Pa using an Instron. The formed tablet is 2.4 cm in diameter and 0.5 cm in height. SEM images of the tablet surface are shown below:

\textsuperscript{1} Duke Scientific Corporation, California, USA
4.4 MOUNTING OF PARTICLE

A single particle, typically 10 - 40 μm in diameter, was selected under an optical microscope and glued to the underside of a commercially available cantilever spring using a commercial two part epoxy resin (Araldite). Manipulation of the particle was performed using a hydraulic micro-manipulator.
To aid visualization of the positioning of the mounted particle on the cantilever spring, a mounting fixture (see Figure 4.3) was assembled, using glass microscope slides. Small quantities of sample particles and adhesive were placed at different locations on a microscope cover slip. The cover slip was then attached to the mounting fixture using Blue Tac to hold it firmly in place and the assembly placed under an optical microscope.

Using the micro-manipulation stage, the AFM cantilever was carefully placed opposite the cover slip, with the tip facing the particles and adhesive. The tip of the cantilever was firstly dipped into the adhesive and then brought into contact with a chosen particle. Horizontal alignment was achieved by placing both the cantilever tip and particle equator in the focal plane of the microscope objective. Once placement of the particle was complete, the system was left to set for at least 24 hours.

The principal advantage of this technique is that particles remain unobscured by the cantilever. This allowed observation of the moment of contact between particle and cantilever, giving greater control over particle location and the amount of adhesive used. This is especially significant for smaller particles below 10 microns in size. Photographs were taken of the cantilever and particle system using an optical microscope and by scanning electron microscopy. The images were used to

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Figure 4.3 Side-view showing particle mounting (not to scale)

To aid visualization of the positioning of the mounted particle on the cantilever spring, a mounting fixture (see Figure 4.3) was assembled, using glass microscope slides. Small quantities of sample particles and adhesive were placed at different locations on a microscope cover slip. The cover slip was then attached to the mounting fixture using Blue Tac to hold it firmly in place and the assembly placed under an optical microscope.

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2 Zeiss Axiotech reflected light microscope
characterise the particle and confirm cantilever dimensions as supplied by the manufacturers.

Figure 4.4 SEM images of the dimensions of AFM cantilever spring to determine the spring constant

Figure 4.5 SEM image of a mounted polystyrene particle on cantilever
4.5 EXPERIMENTAL

4.5.1 AFM Non-Contact scanning

As previously mentioned in Section 2.3.3, the commercial AFM has several modes of operation depending on the information required. The greatest advantage of AFM compared to the custom-built instrument is its ability to scan the topography of the substrate. This is vital to locate smooth regions on the polystyrene tablet for adhesion, applied load and contact time studies. The topography map acquired can be as large as $100 \mu m^2$ or as small as $1 \mu m^2$ in size. Topographical information may be obtained in one of two ways, contact scanning or non-contact scanning. This simply refers to whether or not the scanning probe actually comes into physical contact with the sample surfaces. Non-contact scanning is used in the present work to measure the topography of the polystyrene tablet. This method is favoured over contact imaging to minimise damage to the sample and to avoid detachment of the particle from the cantilever.

Non-contact imaging is typically conducted using a sharp cantilever tip. However, in the present adhesion investigations, the imaging is conducted using a particle attached to the end of the cantilever using the method described in Section 4.4. Imaging with an attached particle facilitates alignment of the particle with smooth regions of the tablet when adhesion measurements are taken. Accurate alignment of the probe particle with a specific particle on the surface also avoids multi-particle contacts which would occur of the probe particle landed at the boundary between particles in the tablet. For nanoindentation studies, a sharp cantilever was used, for non-contact imaging and nanoindentation using the same principle.

In non-contact operation, the cantilever is oscillated at its resonant frequency. In this mode, what is being detected is changes in force between the tip and sample. These force changes are also referred to as the force gradient. As the probe gets closer to the sample, the force gradient changes, thus changing both the oscillation amplitude and phase of the vibrating cantilever. Either the change in amplitude or the change in phase can be detected and used to control the tracking of the probe over the surface.
and therefore map the topographic data. In the present work, the non-contact scanning mode with amplitude detection has been used.

Topography scanning is conducted before and after each set of adhesion experiments. The topography map of the polystyrene tablet is acquired at ambient relative humidities whilst smooth regions are located on the tablet. The cantilever and the attached particle are then positioned above the selected region and the humidity inside the AFM chamber is controlled remotely and left to equilibrate for 24 hours before the first force curve is taken. After the adhesion experiments are completed, the chamber is opened for a few hours before another topography map of the tablet is acquired. Repeated imaging ensures that the position of the contact region has not shifted during experimentation. Any changes to the polystyrene tablet as a result of the adhesion studies can also be detected.

Examples of topography scans on the polystyrene tablet are shown below:

Figure 4.6 Topography scan of polystyrene tablet taken with a 12 \( \mu m \) attached polystyrene particle for applied load studies at low relative humidities (PsAl_2) with non-contact imaging.

This 80 \( \mu m \times 80 \mu m \), 200 line resolution non-contact topography scan of the polystyrene tablet is taken at ambient conditions with a 12 \( \mu m \) polystyrene particle attached to a cantilever for the PsAl_2 applied load study. This is a novel technique which does not seem to have been reported in any published literature. The image on the left shows the topography of the substrate and the intensity of the shades denotes the depth profile of the image. For example, the lighter shades show that the highest
point on the scan measures to 7.42 μm. The image on the right is processed by placing an artificial light source on the right hand side of the image. This helps identify the smooth and rough regions on the polystyrene tablet. The image was captured using a scan speed of 20 μm/s and PID settings are adjusted for minimal noise.

Figure 4.7 Topography scan of polystyrene tablet taken with a bare silicon tip for nanoindentation studies with non-contact imaging

This 50 x 50 μm non-contact topography scan of the polystyrene tablet was taken prior to nanoindentation tests at low relative humidities. A bare silicon tip with a spring constant of 11 N/m was used to acquire the scans above. The scans were taken at a resolution of 200 lines and the scan speed used was 25 μm/s.

4.5.2 Point spectroscopy for adhesion and nanoindentation studies

Another feature of the AFM is point spectroscopy, also called deflection-distance or D/S curve acquisition. This mode is used in all the adhesion investigations using the AFM in the present work. In point spectroscopy, the probe is positioned at a point on or above the sample, determined from the topographical scan previously described. The probe is then pushed a pre-set distance towards or into the sample by the movement of the z-piezo. As the distance between the probe and sample decreases, the deflection of the cantilever probe increases. The measured deflection results in a plotted curve of the sensor output (cantilever deflection in nA) versus z-piezo movement, in nanometres (e.g. Figure 4.8).
To acquire a force-distance curve using the AFM, the following input settings have to be set:

**Z-speed**- Sets the approach and retraction speed of the z-piezo. This parameter is important when studying samples, which may exhibit strain-rate dependent behaviour.

**Z-start**- sets the height, relative to the feedback position, where the measurement will begin.

**Z-end**- sets the height, relative to the feedback position, to stop the force-distance measurement.

**Force limit**- sets the sensor value at which the downward motion of the z-piezo will stop. This corresponds directly to the amount of cantilever deflection and therefore the applied load on the sample (this value can be adjusted between -64 to +64 nA).

In adhesion studies, the **Z-end** parameter is set to zero which corresponds to the feedback position of the cantilever. This ensures the particle attached to the cantilever is not indenting into the sample and the applied load on the sample is low. When taking force-curves for nanoindentation studies, the **Z-end** is set to 1000 nm and the **force-limit** is increased gradually to the maximum value of +64 nA. This setting instructs the indentation into the sample to stop when the piezo has travelled 1000 nm into the sample or when the current measurement (in nA) from the photodetector reaches the **force limit**. By setting the **force limit** at a low value, a smaller applied load is applied on to the surface and the indentation depth will be smaller compared to a high **force limit**.

### 4.5.3 Adhesion studies

Experimental studies on the effect of relative humidity on the force of adhesion for polystyrene particles were performed using the custom-built force instrument and the commercial AFM (described in Chapter 3). The humidity was controlled by blending
dry and water-saturated air streams in the correct proportions. Air humidification was achieved using a Dreschl bottle.

Measurements of humidity and temperature were made using a Vaisala HMP 35 probe, with the sensor sited approximately 30 mm from the particle and substrate. An allowance of 5 - 10 minutes was made for the system to reach equilibrium after a change in RH. A study of the time required for the adsorption of moisture to reach an equilibrium state was conducted using the AFM Explorer which allows the same position on the compact to be pin-pointed and revisited. A 12 µm diameter polystyrene particle attached to an AFM cantilever and a polystyrene compact were subjected to a relative humidity of 40% (near ambient conditions) for 48 hours prior to force measurements being taken. The same polystyrene particle and polystyrene compact were then exposed to dry air for 24 hours. The relative humidity was then increased to 40% in 20 minutes. Ten force curves were captured and the adhesion forces measured in the two studies were compared. The results, shown in Table 4.1, indicate little variation in the adhesion forces measured.

Table 4.1 Equilibrium study on polystyrene surfaces

<table>
<thead>
<tr>
<th>System</th>
<th>Mean adhesion force measured (nN)</th>
<th>Standard deviation (nN)</th>
<th>Number of readings</th>
</tr>
</thead>
<tbody>
<tr>
<td>48 hours at 40%RH</td>
<td>741.72</td>
<td>56.25</td>
<td>10</td>
</tr>
<tr>
<td>24 hours at 0.5%RH →40%RH in 20 mins</td>
<td>704.87</td>
<td>46.43</td>
<td>10</td>
</tr>
</tbody>
</table>

In the adhesion studies, both the particle and the substrate were subjected to a series of adsorption and desorption experiments in which the relative humidity was ramped up and down over intervals, for instance 5% RH. Three to eight force curves were then obtained at each relative humidity interval.
4.6 Extraction of adhesive force from raw data

The adhesive force between the particle and substrate is given by the maximum deflection of the cantilever prior to detachment (or decoupling) of the two surfaces. On a force-separation curve this is represented by the minimum in the withdrawal curve. Using HPVEE software written for the custom-built instrument, raw data are acquired in the form of detector voltage versus piezo displacement. Similarly, raw data are acquired in the form of detector current versus piezo displacement in the commercial AFM. The raw data from both instruments are then converted to give the force and true separation distance between the particle attached to the cantilever and the substrate. The conversion process of the raw data for both instruments is identical and to avoid repetition, only the methodology for the custom-built instrument is presented here. This section describes how this process is performed.

The raw data from the HPVEE data acquisition routine can be transported into a spreadsheet format as depicted below in Figure 4.8. The data are taken from the interaction between a flat silicon wafer and a silicon probe tip under ambient conditions to minimise sample and tip deformations and the effects of high relative humidities.

Figure 4.8 Experimental data as exported from the HPVEE data acquisition routine
A mean value of the detector voltage corresponding to data outside the region of particle-surface interaction is taken to give a 'zero force' voltage. In the example given above, the zero force voltage is approximately -3.5V. The value of the zero force voltage is dependent upon the location of the reflected laser spot from the cantilever beam on to the PSD. The data are then shifted on the y-axis so that the zero-force voltage corresponds to a voltage of zero (Tyrrell, 1999). The result of this shift is as follows:

Figure 4.9 Experimental data with 'zero-force' voltage correction applied.

When the cantilever and sample are in contact, the cantilever displacement is synonymous with the displacement of the substrate on the piezo ceramic providing the contact is rigid. Therefore, the cantilever displacement can be obtained by multiplying the detector voltage by the reciprocal of the gradient of the solid-solid contact region using a non-compliant system, e.g. a bare silicon tip on silicon surface.

In order to plot the force of the interaction between the cantilever and the sample and the displacement between the surfaces, the true separation between the surfaces needs to be evaluated. This can be obtained by taking into account the relative movements of the piezo and the cantilever. It is convenient to define a datum as the initial separation, as shown in Figure 4.10. The force acting on the cantilever can be calculated using Hooke's Law (Equation 3.1) by multiplying the cantilever displacement by the spring constant.
Figure 4.10 Diagram depicting the process of extraction of raw data into force vs. true separation curves

Gradient of contact region $= \frac{\Delta \text{Detector voltage}(V)}{\Delta \text{Piezo displacement}(nm)}$

Cantilever displacement (nm) = Zero – force detector voltage * $\frac{1}{\text{Gradient of contact region}}$

True separation (nm) = (Piezo displacement + Cantilever displacement) – Initial separation

Force (N) = Cantilever displacement * Cantilever spring constant

The force-distance curve can be generated as below:
Figure 4.11 A force-separation curve analysed from raw experimental data
4.7 Extraction of force-indentation from raw data for nanoindentation studies

In a nanoindentation test, force-distance curves are acquired using Point Spectroscopy as previously mentioned. The raw data generated by the AFM takes the form of piezo distance (nm) versus cantilever deflection (nA) and the conversion to force versus distance is performed using the method described in Section 4.6. However, unlike the adhesion studies where no indentation occurs, in a nanoindentation test, the indentation depth of the cantilever into the surface has to be analysed from the force-distance curves. Hence, the point on the curve at which the indentation begins has to be determined. Indentation of the tip into the sample is deemed to start at the point where the tip is first brought into contact with the sample and before the Z-piezo exerts any additional load to the sample. At this point zero applied load would be subjected to the sample and loading due to attractive forces such as van der Waals forces will be ignored. This point is depicted in Figure 4.12. The $x$-coordinate at this point is then subtracted from the cantilever deflection raw data to give the corrected raw cantilever deflection values. Similarly, the $y$-coordinate is subtracted from the raw piezo displacement data, thus giving the corrected raw piezo displacement values. Due to the arbitrary signs assigned to piezo displacement (which has an inherent negative sign), the indentation depth comes out to be negative, thus the absolute value is taken so as to represent the indentation depth. A corrected force-depth curve is showed in Figure 4.13.

Figure 4.12. The identification of the starting point for a nanoindentation test
Figure 4.13 Results of a nanoindentation test after the determination of the starting point and the correction of signage
CHAPTER 5 RESULTS

5.1 INTRODUCTION

This chapter details results of experimental studies obtained using single polystyrene particles interacting on a polystyrene substrate acquired from the custom-built force measuring instrument described in Chapter 3 and the Atomic Force Microscope described in Chapter 4. Although the operating principles of both instruments are inherently the same, using the custom-built force instrument, the location for force measurements cannot be viewed and selected, whilst with the AFM, it is possible to select specific contact sites for force measurement by pre-scanning thus multiple contacts between the probe particle and the substrate particles can be avoided. The experimental details and the format of the presented data will also be explained in this chapter.

The effects of relative humidity and applied load on the force of adhesion between the polystyrene surfaces are discussed and analysed. Experimental studies were also conducted for the effect of contact time on the adhesion of the interacting species. In order to assess the effect of relative humidity on the mechanical properties of the polystyrene substrate, the hardness and Young's modulus of the polystyrene substrate were directly measured using nanoindentation. These results are presented in Section 5.6.

The errors associated with the evaluation of cantilever spring constant are analysed based on the resolution of the imaging technique (optical microscopy or scanning electron microscopy), using a propagation method (see Appendix 3).
5.2 EXPERIMENTAL DETAILS

A spherical cross-linked polystyrene particle\(^1\) of 12-14\(\mu\)m in diameter was mounted on to the back of an AFM cantilever spring. The particle is attached on to the cantilever spring using a commercial two-part epoxy resin (Araldite). Manipulation of the particle was performed using a hydraulic micro-manipulator under a high resolution optical microscope. The cantilever with the particle attached was then left to set in an enclosed chamber for at least 24 hours prior to measurements. For the purpose of this study, no special preparation or pre-treatment was used for the particles.

Compacted polystyrene tablets were formed by compressing 2 grammes of polystyrene particles at \(1.08 \times 10^8\) Pa using an Instron. The formed tablet is 2.4 cm in diameter and 0.5 cm in height. SEM images of the tablet are shown in Figures 4.1 and 4.2 in Section 4.3.

Experimental studies of the effect of relative humidity on the force of adhesion for polystyrene particles were performed using the custom-built force instrument and the Atomic Force Microscope (AFM Explorer). In the earlier experiments using the custom-built force instrument, the relative humidity was controlled using either a beaker of distilled water or a tray of silica gel placed inside the enclosing chamber. In experiments conducted with the AFM, the relative humidity in the chamber was controlled by blending streams of dry and saturated air in the desired proportions. Dry air was obtained from a commercial air dryer\(^2\), and saturated air was obtained by routing a proportion of the dry air through a Dreschel bottle. The desired RH was obtained by blending the dry and wet air streams in the appropriate proportions. In the latter method, the environment inside the chamber was controlled with a greater degree of accuracy. A small electric fan was also positioned inside the chamber to assist the mass transfer of water vapour. The fan and the dry air could be operated remotely and were turned off when recording force curves.

\(^1\) Duke Scientific, California, U.S.
\(^2\) Peak Scientific
Chapter 5 Results

Measurements of humidity and temperature were made using a Vaisala HMP 35 probe, with the sensor sited approximately 30 mm from the particle and substrate. An allowance of 5 - 10 minutes was made for the system to reach equilibrium after a change in RH. This was justified by results obtained from a test, which showed a rapid response of adhesion measurement to a step change in relative humidity (see Section 4.5.3).

5.3 APPLIED LOAD STUDIES

The influence of applied load on the force of adhesion was investigated for the polystyrene system. The study was carried out at low, medium and high relative humidities. Evidence from literature suggests that there is little influence of applied load on adhesive force in ambient conditions. Schaefer et al. (1994) reported that under the maximum load of 50 nN from a rigid flat surface, a 5 µm polystyrene particle deformed by 50 nm. An identical study on a 7 µm particle yielded a less pronounced influence of applied load. In a later study, Schaefer et al. (1995) measured the pull-off forces of an 8 µm polystyrene sphere interacting with a graphite surface and found that the pull-off forces were constant for the range of loading between 40-410 nN. No reported literature was found on the effect of applied loads on the force of adhesion at higher humidities.

The applied load experiments were conducted using a 12-14 µm polystyrene particle mounted on a cantilever spring interacting on a polystyrene tablet. The spring constant of the cantilever was calculated using the Classical Beam Theory (see Section 2.4.1) and its dimensions were characterised using scanning electron microscopy. A fresh polystyrene particle was mounted on to a new cantilever spring for each relative humidity to eradicate ambiguities of measured adhesion forces if the polystyrene particle is deformed plastically in the course of experimentation. The applied load experiments were first conducted using the custom-built instrument but later repeated using the AFM. In the custom-built instrument, the applied load was increased by using the z motor driver controller. Once contact between the particle and substrate had been observed, a force curve was acquired. When the particle and substrate had cycled out of contact, the motor controller was driven incrementally in the z-direction.
to decrease the absolute separation between the particle and the substrate. With the piezo displacement being a constant parameter, a higher compressive load occurs between the particle and substrate when contact is made. In the AFM, the applied load was controlled by setting a higher set-point parameter, which corresponds to the maximum deflection of the cantilever spring after contact has been made. The higher the set-point, the greater the cantilever deflection which translates to a higher applied load on the substrate. The magnitude of applied load corresponds to the highest value of force registered during contact, e.g. 703 nN as illustrated in Figure 5.2. Force curves were captured at various applied loads and three or five sets of data were acquired at each load. Typical force curves at low RH and high RH are shown in Figure 5.2 to Figure 5.5.
5.3.1 Applied load experiment of a polystyrene particle on polystyrene tablet using the custom-built instrument

Particle size and surface preparation technique
12 μm diameter cross-linked (1%DVB) polystyrene particle as received
2.4 cm diameter cross-linked (1%DVB) polystyrene tablet compacted at 1.08 x 10^8 Pa

Experiment reference: PsAl_1

Cantilever data (dimensions measured by optical microscopy)

<table>
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<tr>
<th></th>
<th>180 μm ± 1 μm</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Length</strong></td>
<td></td>
</tr>
<tr>
<td><strong>Width</strong></td>
<td>20 μm ± 1 μm</td>
</tr>
<tr>
<td><strong>Thickness</strong></td>
<td>2 μm ± 1 μm</td>
</tr>
<tr>
<td><strong>Shape</strong></td>
<td>Triangular</td>
</tr>
<tr>
<td><strong>Young's modulus</strong></td>
<td>(1.71 \times 10^{11} \text{ Nm}^{-2} \pm 3.42 \times 10^{10} \text{ Nm}^{-2})</td>
</tr>
<tr>
<td><strong>Calculated spring constant</strong></td>
<td>(2.34 \text{ Nm}^{-1} \pm 0.3987 \text{ Nm}^{-1})</td>
</tr>
</tbody>
</table>

Comments

The results (Figure 5.1) indicate that at low humidities, i.e., 14% and 30% RH, the force of adhesion was unaffected by increasing the applied load. There has been no literature found which reports the influence of applied load on the adhesive force of polystyrene particles with varying relative humidities. All the past studies on the effect of applied load on polystyrene have been conducted under ambient conditions where there was little dependency on the applied load found on the adhesive force (Schaefer et al., 1994, 1995). At low humidities, this concurs with the present results.

At 60% RH, the adhesion force increased steadily with increasing applied load. There was also evidence of liquid bridge elongation from the force curves at this relative humidity, which suggests that capillary effects were taking place between the interacting polystyrene particle and polystyrene tablet (Figure 5.4 & 5.5). The distinct influence of applied load on the adhesive force at this humidity indicates that effects

* The uncertainty in the Young's modulus of the spring constant is based on 20% of the typical value (Sader, 1995).
such as softening and deformation of the material may be occurring. This phenomenon will be further addressed in Chapter 7.

Figure 5.1 Effect of applied load on the force of adhesion of a polystyrene particle interacting with polystyrene tablet measured using the custom-built instrument at various relative humidities (PsAl_1)
Figure 5.2 Interaction between a 12 μm diameter PS particle and a PS tablet at 14% RH, at low applied load (PsAl_1)

Figure 5.3 Interaction between a 12 μm diameter PS particle and a PS tablet at 14% RH, at high applied load (PsAl_1)
Figure 5.4 Interaction between a 12 μm diameter PS particle and a PS tablet at 60% RH, at low applied load (PsAl_1)

Figure 5.5 Interaction between a 12 μm diameter PS particle and a PS tablet at 60% RH, at high applied load (PsAl_1)
5.3.2 Applied load experiment of a polystyrene particle on polystyrene tablet using the AFM Explorer

Particle size and surface preparation technique
12 μm diameter cross-linked (1% DVB) polystyrene particle as received
2.4 cm diameter cross-linked (1% DVB) polystyrene tablet compacted at 1.08 x 10^8 Pa

Experiment reference: PsAl_2

Cantilever data (dimensions measured by scanning electron microscopy)

<table>
<thead>
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<th></th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Length</td>
<td>86 μm ± 0.5 μm</td>
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<td>Width</td>
<td>60 μm ± 0.5 μm</td>
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<td>Thickness</td>
<td>1.6 μm ± 0.1 μm</td>
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<tr>
<td>Shape</td>
<td>Rectangular beam</td>
</tr>
<tr>
<td>Young's modulus</td>
<td>1.71 x 10^{11} Nm^{-2} ± 3.42 x 10^{10} Nm^{-2}</td>
</tr>
<tr>
<td>Calculated spring constant</td>
<td>16.51 Nm^{-1} ± 2.44 Nm^{-1}</td>
</tr>
</tbody>
</table>

Comments
In this applied load study, the experiments were conducted using the AFM Explorer at 1% RH, 35% RH and 65% RH. A 12 μm polystyrene particle was attached to a 16.5 N/m spring cantilever. The adhesion forces of the same particle and cantilever interacting on the same contact spot on the polystyrene tablet were measured at the three relative humidities. The range of applied loads varied from 200 nN up to approximately 4000 nN. The results (shown in Figure 5.6) are consistent with PsAl_1 whereby at low relative humidities, the adhesion forces measured showed little variation with the increasing applied load.

The effect of applied load on the adhesion forces between the polystyrene surfaces is clearly visible at 65% RH. There seems to be a transition period at 1000 nN when the adhesion force begins to increase steadily as the applied load increases. This transition may be an indication of the onset of elasto-plastic deformation of the surfaces and this point will be further examined in Chapter 7. The fact that this marked effect of applied load on the adhesion forces of the polystyrene surfaces at high relative
humidities is reproducible using two different instruments indicates that this is a real phenomenon and not an artifact of the measuring device.

The force curves captured at 1% RH and 65% RH at low loads (Figure 5.7 and 5.9) show no sign of non-elastic deformation at the contact regions. This is observed from the perfectly superimposed approach and withdrawal curves in the contact region, when separation between the particle and substrate is zero. At high applied loads, even at 1% RH (Figure 5.8), the surfaces in contact are beginning to exhibit significant elastic deformation, corresponding with the non-linear but superimposing approach and withdrawal curves. At high RH (Figure 5.10), the approach and withdrawal curves no longer superimpose on to each other and this is an indication of non-elastic deformation.

Figure 5.6 Effect of applied load on the force of adhesion of a polystyrene particle interacting with polystyrene tablet measured using the AFM Explorer at various relative humidities (PsAI_2)
Figure 5.7 Interaction between a 12 μm diameter PS particle and a PS tablet at 1% RH, and low applied load (PsAl_2)

Figure 5.8 Interaction between a 12 μm diameter PS particle and a PS tablet at 1% RH, and high applied load (PsAl_2)
Figure 5.9 Interaction between a 12 μm diameter PS particle and a PS tablet at 65% RH, and low applied load (PsAl_2)

Figure 5.10 Interaction between a 12 μm diameter PS particle and a PS tablet at 65% RH, and high applied load (PsAl_2)
5.3.3 Applied load experiment of a polystyrene particle on polystyrene tablet using the AFM Explorer (high loads)

Particle size and surface preparation technique
14 µm diameter cross-linked (1%DVB) polystyrene particle as received
2.4 cm diameter cross-linked (1%DVB) polystyrene tablet compacted at 1.08 x 10^8 Pa

Experiment reference: PsAl_3

Cantilever data (dimensions measured by scanning electron microscopy)

<p>| | |</p>
<table>
<thead>
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<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Length</td>
<td>165 µm ± 0.5 µm</td>
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<td>Width</td>
<td>50 µm ± 0.5 µm</td>
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<tr>
<td>Thickness</td>
<td>5.2 µm ± 0.1 µm</td>
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<tr>
<td>Shape</td>
<td>Rectangular beam</td>
</tr>
<tr>
<td>Young's modulus</td>
<td>1.71 x 10^{11} Nm^{-2} ± 3.42 x 10^{10} Nm^{-2}</td>
</tr>
<tr>
<td>Calculated spring constant</td>
<td>66.9 Nm^{-1} ± 7.06 Nm^{-1}</td>
</tr>
</tbody>
</table>

Comments

This study was carried out to investigate the reversibility of the effect of applied load on the adhesion forces of the polystyrene surfaces at high RH. In the previous two studies (PsAl_1 and PsAl_2), force curves were taken starting with low applied loads followed by a gradual increase in the applied load. In this study, the force curves were captured at 65% RH from applied loads ranging from 4 pN to about 31 pN. Using the same particle and cantilever at the same position on the tablet, force curves were then captured from high applied loads followed by a gradual decrease to the lower applied loads at about 4 pN.

The results depicted in Figure 5.11, show a gradual increase of measured adhesion force between the polystyrene surfaces as the applied load was increased from 4 µN to 31 µN. At such high applied loads, the polystyrene surfaces are likely to undergo plastic deformation which leads to a permanent increase in contact area between the surfaces and therefore increased adhesion forces. This was confirmed when force curves taken in descending order of applied load (from high applied load to low applied load) show a significant increase in the measured adhesion forces compared to
the ascending order of applied load. Upon decent back to an applied load of 4 μN, the adhesion forces have increased by 4-fold compared to the adhesion observed at 4 μN applied load before the load was increased. This is due to the fact that in the earlier experiments (ascending order of applied load) the contact region between the particle and the substrate has already been deformed plastically. The high applied loads and high relative humidities are also likely to have flattened out surface asperities both on the particle and the substrate, yielding a larger contact area and increasing the solid-solid interaction between the surfaces. When further force curves were taken, even at the same applied load, the contact area of the surfaces has been significantly increased, which leads to the increased adhesion forces. The increment of adhesion forces with the descending order of applied loads is an indication that further plastic deformation may be occurring at the polystyrene surfaces. The results of this study will be discussed in greater detail in Chapter 7.

With an applied load of 15 μN at 65% RH (Figure 5.12), the force curve already exhibits non-elastic deformation at the contact region. As the applied load was further increased to 31 μN, the contact region of the surfaces exhibit clear non-linear characteristics (Figure 5.13 & 5.14). When the applied load was decreased to 4 μN, the adhesion forces measured increased by a magnitude of four as compared to the results obtained at the start of the test before the applied load was increased. However, at this load, there is little evidence of plastic deformation from the force curve in Figure 5.15.
Figure 5.11 Hysteresis of the adhesion force as a function of applied load between the polystyrene surfaces at 65% RH (PsAl_3)
Figure 5.12 Interaction between a 14 \( \mu \)m diameter PS particle and a PS tablet at 65% RH, and low applied load (increasing applied load PsAl_3)

Figure 5.13 Interaction between a 14 \( \mu \)m diameter PS particle and a PS tablet at 65% RH, and high applied load (increasing applied load PsAl_3)
Figure 5.14 Interaction between a 14 μm diameter PS particle and a PS tablet at 65% RH, and high applied load (decreasing applied load PsAl_3)

Figure 5.15 Interaction between a 14 μm diameter PS particle and a PS tablet at 65% RH, and low applied load (decreasing applied load PsAl_3)
5.4 ADHESION STUDIES

Studies on the effect of relative humidity on the adhesion force were carried out on the cross-linked polystyrene particles interacting on the polystyrene tablet. The investigation was conducted using the custom-built instrument and the AFM Explorer. Using the AFM Explorer, the topography of the PS tablet is mapped and the exact location of force-measurements on the tablet can be pin-pointed.

5.4.1 Polystyrene particle on polystyrene tablet using the custom-built instrument (PsAd_1)

Particle size and surface preparation technique

12 μm diameter cross-linked (1%DVB) polystyrene particle as received
2.4 cm diameter cross-linked (1%DVB) polystyrene tablet compacted at 1.08 × 10^8 Pa

Experiment reference: PsAd_1

Cantilever data (dimensions measured by optical microscopy)

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Length</td>
<td>180 μm ± 1 μm</td>
</tr>
<tr>
<td>Width</td>
<td>20 μm ± 1 μm</td>
</tr>
<tr>
<td>Thickness</td>
<td>2 μm ± 1 μm</td>
</tr>
<tr>
<td>Shape</td>
<td>Triangular</td>
</tr>
<tr>
<td>Young's modulus</td>
<td>1.71 x 10^{11} Nm^{-2} ± 3.42 x 10^{10} Nm^{-2}</td>
</tr>
<tr>
<td>Calculated spring constant</td>
<td>2.34 Nm^{-1} ± 0.398 Nm^{-1}</td>
</tr>
</tbody>
</table>

Comments

In this study, the particle and compact were subjected to adsorption of water from air at 1.5% RH to 75% RH, at increments of 5% RH (see Figure 5.16), followed by desorption of moisture, from 75% RH to 5% RH (see Figure 5.17). Five sets of data were taken for each relative humidity.
The applied loads at which the experiments were carried out ranged from 300 nN to 3000 nN. This parameter could not be set to a definite value using the custom-built instrument.

In the adsorption cycle, shown as Figure 5.16, the force of adhesion showed little variation as the relative humidity was increased from 1.7% RH to 60% RH. From 60% RH onwards, the adhesive force sharply increased and then appeared to drop slightly at 75% RH but regained to 2300 nN at 80% RH.

The applied load in the region of 60% RH to 80% RH ranges from 1000 nN to over 3000 nN, and from Section 5.3, the applied load clearly affects the magnitude of adhesive force at high relative humidities. This may explain the scatter in the data points in the region of 60% RH to 80% RH in Figure 5.16 and 5.17.

In the desorption cycle, shown in Figure 5.17, the adhesion force was slightly lower by 400 nN in magnitude at the higher humidities (60% to 75%) and a noticeable peak was observed at 45% RH. From 35% RH down to 1% RH, the adhesive forces obtained were in close agreement compared with the results from the adsorption cycle.

In the sequence of force curves in the adsorption cycle shown as Figures 5.18, 5.19 and 5.20, hysteresis in the solid-solid contact region significantly increased as the relative humidity was increased. The hysteretic phenomenon was slightly diminished, although not completely absent when the polystyrene particle and tablet were desorbed to 1%RH (Figure 5.23). This suggests a non-elastic contact between the particle and substrate contact region, which is not reversible over the timescales studied.
Figure 5.16 Effect of increasing RH on the adhesive force of 12 μm diameter PS particle interacting with PS tablet (PsAd_1)
Figure 5.17 Effect of decreasing RH on the adhesive force of 12 \( \mu m \) diameter PS particle interacting with PS tablet (PsAd_1)

Figure 5.18. Interaction between a 12 \( \mu m \) diameter PS particle and a PS tablet at 11\% RH in the adsorption sequence (PsAd_1)
Chapter 5 Results

Figure 5.19 Interaction between a 12 μm diameter PS particle and a PS tablet at 35.4 % RH in the adsorption sequence (PsAd_1)

![Graph showing interaction between a 12 μm diameter PS particle and a PS tablet at 35.4 % RH.](image1)

Figure 5.20 Interaction between a 12 μm diameter PS particle and a PS tablet at 60.2% RH in the adsorption sequence (PsAd_1)

![Graph showing interaction between a 12 μm diameter PS particle and a PS tablet at 60.2% RH.](image2)
Figure 5.21 Interaction between a 12 \( \mu \text{m} \) diameter PS particle and a PS tablet in the desorption sequence at 60.6\% RH (PsAd_1)

![Graph showing interaction force vs. separation](image1)

Figure 5.22 Interaction between a 12 \( \mu \text{m} \) diameter PS particle and a PS tablet in the desorption sequence at 40.4\% RH (PsAd_1)

![Graph showing interaction force vs. separation](image2)
Figure 5.23 Interaction between a 12 μm diameter PS particle and a PS tablet in the desorption sequence at 20.4% RH (PsAd_1)

Figure 5.24 Interaction between a 12 μm diameter PS particle and a PS tablet in the desorption sequence at 0.9% RH (PsAd_1)
5.4.2 Polystyrene particle on polystyrene tablet using the custom-built instrument (PsAd_2)

Particle size and surface preparation technique
12 μm diameter cross-linked (1%DVB) polystyrene particle as received
2.4 cm diameter cross-linked (1%DVB) polystyrene tablet compacted at 1.08 x 10⁸ Pa

Experiment reference: PsAd_2

Cantilever data (dimensions measured by optical microscopy)

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<tr>
<td>Thickness</td>
<td>2 μm ± 1 μm</td>
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<tr>
<td>Shape</td>
<td>Triangular</td>
</tr>
<tr>
<td>Young's modulus</td>
<td>1.71 x 10¹¹ Nm⁻² ± 3.42 x 10¹⁰ Nm⁻²</td>
</tr>
<tr>
<td>Calculated spring constant</td>
<td>2.34 Nm⁻¹ ± 0.398 Nm⁻¹</td>
</tr>
</tbody>
</table>

Comments

In this series of experiments, the desorption cycle was performed before the adsorption cycle. Three force curves were captured for each relative humidity in the range of 1% to 75%, at increments of 5%. All the force curves captured in this study were acquired at applied load of 400 nN to 3500 nN.

Results from the desorption of the particle and tablet showed a high adhesion force at 60% RH before decreasing to a fairly constant force of adhesion from 55% RH to 1% RH (Figure 5.25). The adsorption curve, presented as Figure 5.26, is in very good agreement with data obtained in the desorption series. The force of adhesion sharply increased to a peak value of 4500 nN at 70% RH.
The series of force curves captured in the desorption and adsorption sequence (Figures 5.27 to 5.32) exhibit hysteretic effects in the contact region reminiscent of plastic deformation behaviour. The force curves taken at high relative humidities (Figure 5.27 and 5.32) also suggest capillary condensation to be occurring at the surfaces due to the large adhesion forces and the high separation distances after pull-off.

Figure 5.25 Effect of decreasing RH on the adhesive force of 12µm diameter PS particle interacting with PS tablet (PsAd_2)
Figure 5.26 Effect of increasing RH on the adhesive force of 12\(\mu\)m diameter PS particle interacting with PS tablet (PsAd_2)

![Graph showing the effect of relative humidity on adhesive force](image)

Figure 5.27 Interaction between a 12 \(\mu\)m diameter PS particle and a PS tablet in the desorption sequence at 60.9\%RH (PsAd_2)

![Graph showing interaction force vs. distance](image)
Figure 5.28 Interaction between a 12 μm diameter PS particle and a PS tablet in the desorption sequence at 30.2%RH (PsAd_2)

Figure 5.29 Interaction between a 12 μm diameter PS particle and a PS tablet in the desorption sequence at 5.8%RH (PsAd_2)
Figure 5.30 Interaction between a 12 μm diameter PS particle and a PS tablet in the adsorption sequence particle and PS tablet in adsorption sequence at 1.9%RH (PsAd_2)

Figure 5.31 Interaction between a 12 μm diameter PS particle and a PS tablet in the adsorption sequence particle and PS tablet in adsorption sequence at 34.5%RH (PsAd_2)
Figure 5.32 Interaction between a 12 μm diameter PS particle and a PS tablet in the adsorption sequence particle and PS tablet in adsorption sequence at 70.4%RH (PsAd_2)
5.4.3 Polystyrene particle on polystyrene tablet using AFM Explorer (PsAd_3)

Particle size and surface preparation technique
10 μm diameter cross-linked (1%DVB) polystyrene particle as received
2.4 cm diameter cross-linked (1%DVB) polystyrene tablet compacted at 1.08 x 10^8 Pa

Experiment reference: PsAd_3

Cantilever data (dimensions measured by scanning electron microscopy)

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<td>Shape</td>
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<td>Young's modulus</td>
<td>1.71 x 10^{11} Nm^{-2} ± 3.42 x 10^{10} Nm^{-2}</td>
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<tr>
<td>Calculated spring constant</td>
<td>11.7 Nm^{-1} ± 1.63 Nm^{-1}</td>
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Comments

Using the AFM Explorer, the adhesion forces between the polystyrene surfaces were measured at various relative humidities. As previously mentioned, the primary difference between the custom-built instrument and the AFM Explorer in terms of the adhesion studies conducted in this project is the AFM's capability for imaging the surface and locating a smooth region on the polystyrene tablet. The topographical information is useful for the contacting position of the polystyrene particle on the polystyrene substrate for the adhesion experiments.

In this experiment, the relative humidity was increased from 2.6% RH to 65% RH, in 5% RH increments. At each relative humidity, 6 force curves were captured. The results of the adsorption and desorption cycle are shown respectively in Figure 5.33 and Figure 5.34. Unlike PsAd_1 and PsAd_2, the measured adhesion forces did not appear to follow a clear trend as the relative humidity was increased or decreased. In the adsorption cycle (Fig. 5.33), the adhesion forces at low relative humidities (2.6 % RH to 35% RH) are significantly higher compared to the two previous experiments. A likely explanation for this is the reduced effects of surface roughness due to the mapping of the polystyrene substrate topography by the AFM which allows for the selection of a smooth region on the tablet for the experiments to be conducted.
Another key observation from the results of the adsorption and desorption cycles is the spread in the data points. There seemed to be a larger variance in the measured adhesion forces especially at 25% RH in the desorption cycle. The source of the spread in data points is not clear but further statistical analysis will be conducted on the results and shown in Chapter 6.

Force curves in this study were acquired with an applied load of 1500 nN. At low humidities, (2.1% RH in Figure 5.35 and 35% RH in Figure 5.36), this applied load has clearly not affected the contacting surfaces. This inference is drawn from the perfectly linear superimposition of the approach and withdrawal curves. At 64.6% RH (Figure 5.37) the onset of non-elastic deformation can be detected at the contact region on the force curve. This non-elastic deformation is further observed in the desorption cycle when force curves were captured at 63.9% RH (Figure 5.38) and 35% RH (Figure 5.39). At 5.6% RH, the hysteretic effect is absent from the acquired force-curve.
Figure 5.33 Effect of increasing RH on the adhesive force of 10 μm diameter PS particle interacting with PS tablet (PsAd_3)
Chapter 5 Results

Figure 5.34 Effect of decreasing RH on the adhesive force of 10 \( \mu \text{m} \) diameter PS particle interacting with PS tablet (PsAd\_3)

![Graph showing the effect of RH on adhesive force](image)

Figure 5.35 Interaction between a 10 \( \mu \text{m} \) diameter PS particle and a PS tablet in the adsorption sequence particle at 2.1 \%RH (PsAd\_3)

![Graph showing interaction force against separation](image)
Figure 5.36 Interaction between a 10 µm diameter PS particle and a PS tablet in the adsorption sequence particle at 35 %RH (PsAd_3)

Figure 5.37 Interaction between a 10 µm diameter PS particle and a PS tablet in the adsorption sequence particle PS particle and PS tablet at 64.6 %RH (PsAd_3)
Figure 5.38 Interaction between a 10 \(\mu\)m diameter PS particle and a PS tablet in the desorption sequence at 63.9 % RH (PsAd_3)

Figure 5.39 Interaction between a 10 \(\mu\)m diameter PS particle and a PS tablet in the desorption sequence PS particle and PS tablet at 35 % RH (PsAd_3)
Figure 5.40 Interaction between a 10 μm diameter PS particle and a PS tablet in the desorption sequence at 5.6 %RH
5.4.4 Polystyrene particle on polystyrene tablet using AFM Explorer (PsAd_4)

Particle size and surface preparation technique
10 μm diameter cross-linked (1%DVB) polystyrene particle as received
2.4 cm diameter cross-linked (1%DVB) polystyrene tablet compacted at 1.08 x 10⁸ Pa

Experiment reference: PsAd_4

Cantilever data (dimensions measured by scanning electron microscopy)

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<td>Young's modulus</td>
<td>1.71 x 10¹¹ Nm⁻² ± 3.42 x 10¹⁰ Nm⁻²</td>
</tr>
<tr>
<td>Calculated spring constant</td>
<td>11.7 Nm⁻¹ ± 1.63 Nm⁻¹</td>
</tr>
</tbody>
</table>

Comments

The effect of relative humidity on the force of adhesion between a single polystyrene particle and the polystyrene tablet is further investigated using the AFM Explorer. The experiment was carried out with the increase in relative humidity from 4% RH to 65% RH followed by desorption of moisture from 66.5% RH to 5.6 %RH using a 10 μm diameter polystyrene particle mounted on a 11 N/m cantilever spring. At each increment of relative humidity, eight force curves were taken consecutively. The applied load for all the force curves acquired in the adsorption and desorption cycles was kept at 780 nN to minimise any non-elastic deformation effects. The results are shown in Figure 5.41 and Figure 5.42.

In the adsorption cycle (Figure 5.41), the highest adhesion force measured occurred at 10% RH. The adhesional value of 1800 nN at this RH is in the same order of magnitude as previously reported in the PsAd_3 study (refer to Figure 5.33). This value then dropped to around 800 nN when the relative humidity was increased to 15% RH. There seemed to be a gradual increase of adhesion forces when the relative humidity was further increased to 55 % RH.
In the desorption cycle (Figure 5.42), a clearer trend is observed when the relative humidity was decreased from 65% RH to 5% RH. The adhesion forces measured gradually decreased in magnitude from 1400 nN to approximately 600 nN as the relative humidity was decreased from 65% RH to 30% RH. From this point onwards, the adhesion forces rose to the peak value of 1600 nN at 20% RH before dropping to 600 nN at 5% RH. The wide spread of data points at 15% RH is reminiscent of the scatter at 25% RH in PsAd_3.

The sequence of force curves taken in the adsorption cycle (Figures 5.43 to 5.45) indicates an increase in deformation in the contact region as the relative humidity was increased. In the desorption cycle (Figures 5.46 to 5.48), the force curves shown were acquired at 65% RH, 31.2% RH and 10% RH. Even though the relative humidity has been decreased, the contacting surfaces seemed not to regain their rigidity as indicated by the negative slope of the contact region on the force curves.
Figure 5.41 Effect of increasing RH on the adhesive force of 10 μm diameter PS particle interacting with PS tablet (PsAd_4)
Figure 5.42 Effect of decreasing RH on the adhesive force of 10 μm diameter PS particle interacting with PS tablet (PsAd_4)

![Graph showing the effect of decreasing RH on the adhesive force of a 10 μm diameter PS particle interacting with a PS tablet.]

Figure 5.43 Interaction between a 10 μm diameter PS particle and a PS tablet in the adsorption sequence at 9.9 %RH (PsAd_4)

![Graph showing the interaction between a 10 μm diameter PS particle and a PS tablet in the adsorption sequence at 9.9 %RH.]

126
Chapter 5 Results

Figure 5.44 Interaction between a 10 μm diameter PS particle and a PS tablet in the adsorption sequence at 39.3 %RH (PsAd_4)

![Graph showing interaction between a 10 μm diameter PS particle and a PS tablet at 39.3 %RH](image)

Figure 5.45 Interaction between a 10 μm diameter PS particle and a PS tablet in the adsorption sequence at 66.7 %RH (PsAd_4)

![Graph showing interaction between a 10 μm diameter PS particle and a PS tablet at 66.7 %RH](image)
Figure 5.46 Interaction between a 10 μm diameter PS particle and a PS tablet in the desorption sequence PS particle and PS tablet at 65 % RH (PsAd_4)

Figure 5.47 Interaction between a 10 μm diameter PS particle and a PS tablet in the desorption sequence PS particle and PS tablet at 31.2 % RH (PsAd_4)
Figure 5.48 Interaction between a 10 \( \mu \text{m} \) diameter PS particle and a PS tablet in the desorption sequence PS particle and PS tablet at 10\% RH (PsAd_4)
5.4.5 Polystyrene particle on polystyrene tablet using AFM Explorer (PsAd_5)

Particle size and surface preparation technique
10 µm diameter cross-linked (1%DVB) polystyrene particle as received
2.4 cm diameter cross-linked (1%DVB) polystyrene tablet compacted at 1.08 x 10^8 Pa

Experiment reference: PsAd_5

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<td><strong>Young's modulus</strong></td>
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<td><strong>Calculated spring constant</strong></td>
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Comments

In this investigation, a 10 µm diameter polystyrene particle was used. The particle was then mounted on to the back of a 11.7 N/m rectangular spring. The relative humidity was increased from 10% RH to 60% RH in the adsorption cycle and then decreased within the same range of relative humidity in the desorption cycle. Eight individual force curves were taken at each relative humidity. The applied load in all the force measurements in this study was kept at approximately 900 nN.

Figure 5.49 shows the results obtained from the adsorption cycle. At 10% RH, the adhesion forces measured were in the range of 1500 nN which is very similar to the values obtained in the previous two studies (refer to Figure 5.32 and 5.41). The adhesion force then decreased to 800 nN at 15% RH before peaking at 1600 nN at 35% RH.

The trend in the desorption cycle is less apparent. The highest adhesion forces were detected at the lower ranges of relative humidity at 20% RH and 10 % RH. At relative humidities of 25% RH and above, the measured forces were very similar to the values obtained in the adsorption cycle. As the applied load used in this study was low, the
force curves exhibit no hysteretic or non-elastic characteristics in the contact region (Figures 5.51 to 5.56)

Figure 5.49 Effect of increasing RH on the adhesive force of 10 μm diameter PS particle interacting with PS tablet (PsAd_5)
Chapter 5 Results

Figure 5.50 Effect of decreasing RH on the adhesive force of 10 μm diameter PS particle interacting with PS tablet (PsAd_5)

![Graph showing the effect of RH on adhesive force](image)

Figure 5.51 Interaction between a 10 μm diameter PS particle and a PS tablet in the adsorption sequence PS particle and PS tablet in adsorption sequence at 11.3% RH (PsAd_5)

![Graph showing interaction force vs. separation](image)

132
Figure 5.52 Interaction between a 10 μm diameter PS particle and a PS tablet in the adsorption sequence PS particle and PS tablet at 40 % RH (PsAd_5)

![Graph showing interaction between a 10 μm diameter PS particle and a PS tablet at 40 % RH.](image1)

Figure 5.53 Interaction between a 10 μm diameter PS particle and a PS tablet in the adsorption sequence PS particle and PS tablet at 60.6 % RH (PsAd_5)

![Graph showing interaction between a 10 μm diameter PS particle and a PS tablet at 60.6 % RH.](image2)
Chapter 5 Results

Figure 5.54 Interaction between a 10 \( \mu \)m diameter PS particle and a PS tablet in the desorption sequence PS particle and PS tablet at 65.1\% RH (PsAd_5)

Figure 5.55 Interaction between a 10 \( \mu \)m diameter PS particle and a PS tablet in the desorption sequence PS particle and PS tablet at 46\% RH (PsAd_5)
Figure 5.56 Interaction between a 10 μm diameter PS particle and a PS tablet in the desorption sequence PS particle and PS tablet at 16% RH (PsAd_5)
5.4.6 Polystyrene particle on polystyrene tablet using AFM Explorer (PsAd_6)

Particle size and surface preparation technique
10 μm diameter cross-linked (1%DVB) polystyrene particle as received
2.4 cm diameter cross-linked (1%DVB) polystyrene tablet compacted at 1.08 x 10^8 Pa

Experiment reference: PsAd_6

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<td>Young's modulus</td>
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<td>Calculated spring constant</td>
<td>2.93 Nm^{-1} ± 0.388 Nm^{-1}</td>
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Comments

The main objective of this study is to compare the results of force measurements with varying relative humidity between the custom-built instrument and the AFM Explorer. Hence, the topography of the polystyrene tablet was not measured prior to force measurements. A 10 μm diameter polystyrene particle was mounted on to a cantilever with a spring constant of 2.93 N/m. The study was conducted with increasing relative humidity from 1.3 % RH to 67.3 % RH. Six force curves were acquired at each increment of relative humidity.

The results (Figure 5.57) show a remarkable similarity in trend to the results obtained from the custom-built instrument (Figure 5.16 and 5.26). At low relative humidities (1.3% RH to 15% RH), the adhesion forces were approximately in the 500 nN region. From 40% RH onwards, the adhesion force gradually increased to its highest value of 1000 nN at 67.3 %RH. Although the values of adhesion forces measured at high relative humidities were lower compared to the results from PsAd_1 and PsAd_2, the trend of increasing adhesion forces with increasing relative humidity is in close agreement with the two studies.
After the force measurements were completed, the topography of the polystyrene tablet was measured and the location of the force measurements was found to be in the crevice of two larger particles. It is likely that the trend obtained from PsAd_1 and PsAd_2 was also obtained from multiple contacts between the probe particle and substrate particles.

Figure 5.57 Effect of increasing RH on the adhesive force of 10 µm diameter PS particle interacting with PS tablet without topographical measurements (PsAd_6)
5.5 THE EFFECTS OF CONTACT TIME

The effect of contact time between the polystyrene surfaces at different applied loads at high relative humidity was investigated using the AFM Explorer to further validate the hypothesis of non-elastic deformation behaviour of the polystyrene surfaces at high applied loads and high relative humidities. The contact time between the polystyrene particle and the polystyrene substrate is controlled by setting the 'Establish feedback delay parameter' in the AFM software which designates the length of time the polystyrene particle will stay in contact with the polystyrene substrate prior to detachment.

The study comprises three individual sets of experiments conducted at three different applied loads at 380 nN, 1500 nN and 5000 nN. A different polystyrene particle and cantilever spring was used for each of these applied loads. The relative humidity in each experiment was maintained at 65 % RH. The contact time in each experiment was increased from 200 microseconds to 10 seconds, at small increments. At each time interval, five force curves were acquired consecutively.

The results of this study are presented in Figure 5.58. The $x$-axis represents the contact time of the polystyrene surfaces in seconds and the $y$-axis represents the normalised adhesion force, evaluated by dividing the pull-off force by the diameter of the attached polystyrene particle. The measured adhesion forces had to be normalised because the polystyrene particles used at each applied load (low, medium and high) varied in diameter from 10 µm to 12 µm. At low and medium loads, the increase in contact time bears little significance to the measured forces. However, at applied load of 5000 nN the adhesion forces showed a gradual increase as the contact time was above 0.1 seconds. This shows that above the contact time of 0.1 seconds, the polystyrene surfaces adhered more strongly to one another even though the applied load is kept constant. This is further evidence that the polystyrene surfaces are deforming non-elasticity and at longer contact times and at high applied loads and relative humidities, a larger contact area is formed which gives rise to larger adhesion forces. The time dependency of adhesion forces also suggests that the interacting surfaces are exhibiting visco-elastic behaviour.
Figure 5.58 The effect of contact time of polystyrene surfaces at 65 % RH at different applied loads

5.6 NANOINDENATION STUDIES

The primary aim of this experimental study is to evaluate the effect of relative humidity on the mechanical properties of cross-linked polystyrene. Hence, the nanoindentation tests were carried out in two different relative humidities, at 0.1% RH and 65 % RH using the AFM Explorer.

The nanoindentation test involves making a small indent on the surface of a particle in the polystyrene tablet using a sharp probe tip. The depth of the indentation and the load required to make that indentation are obtained from the force-distance curve acquired in the Point-Spectroscopy mode. The procedure for the extraction of raw data into penetration depth versus load is presented in Section 4.6 in the previous
chapter. The indentation depth and load are then subjected to the Oliver-Pharr analysis (Section 2.6) to evaluate the hardness and the Young's modulus of the material.

Silicon AFM cantilever tips were used in the nanoindentation studies. Normally, diamond coated tips are used in nanoindentation work. However, in the present study, the published value of Young's modulus for polystyrene (Rimai et. al. 1994) at 2.6 GPa is considerably lower than the Young's modulus of silicon at 171 GPa. Hence, damage to the tip will be minimal.

Prior to nanoindentation tests, the topography of the substrate is mapped using non-contact imaging to minimise damage to the sample and tip. The sites for the indentations are then selected. Once an indentation has been made, a new location on the substrate is chosen for the next indentation. The penetration depth is varied by changing the 'Force limit parameter' in the Point Spectroscopy settings. The Z-end parameter which sets the height, relative to the feedback position, to stop the force-distance measurement is set to 1000 nm and the force-limit is increased gradually to the maximum value of +64 nA. This setting instructs the indentation into the sample to stop when the piezo has travelled 1000 nm into the sample or when the current measurement (in nA) on the photodetector reaches the Force limit. When the force limit is set at a low value, a smaller applied load is applied on to the surface and the indentation depth will be smaller compared to a high force limit.

The approaching rate of the tip into the sample is set by predefining the 'Sample point' criteria in the Point Spectroscopy settings. This value is set to 0.1 μm/s, which corresponds to loading rate of 148 nN per second. This is in accordance to the procedure published by Oliver and Pharr (1992). The authors measured the load versus indentation curves using quartz, sapphire and tungsten with a loading rate of 185 nN per second for a maximum load of 4.4 mN. In the present work, the maximum load applied to the polystyrene sample is 2.5 mN. The contact time between the probe tip and the sample is set to 1 second, which allows for the elastic recovery of the material and for any time dependent plastic effects to diminish.
The shape of the probe tip has a direct impact on the analysis of the raw data. Excessive damage to the tip would severely affect the evaluated hardness of the material as a significant increase in projected tip area would result from the tip-blunting. A blunted tip would give lower values of hardness compared to a very sharp tip for the same indentation depth. Therefore, the shape and condition of the tip before and after nanoindentation tests needed to be known. This was achieved by high resolution scanning electron microscopy (SEM). The SEM images of the tips used in the two experiments at 0.1% RH and 65% RH before and after the nanoindentation tests are shown below.

Figure 5.59 SEM images of probe tip before and after nanoindentation tests at 0.1% RH

Before

After

Figure 5.60 SEM images of probe tip before and after nanoindentation tests at 65% RH

Before

After
Chapter 5 Results

The SEM images shown in Figures 5.59 and 5.60 indicate that a minimum amount of tip-blunting occurred as a result of the nanoindentation tests at both relative humidities. The minimal amount of damage to the tip justifies the use of silicon tips instead of diamond coated tips. The images also clearly illustrate the conical shape of the probe tips. The spring constant of the tips are determined from the dimensions of the tip using the loaded beam theory (Section 2.4.3).

Following the analysis of Oliver and Pharr (1992) previously described in Section 2.6, the unloading stiffness of each nanoindentation force-curve is evaluated by taking the gradient of the unloading curve. The contact depths of the indentations denoted by $h_c$, are then calculated based on Eqn. 2.29. The projected area of the indentation, $A$, is estimated by evaluating the indenter shape function at the contact depth $h_c$, that is $A = f(h_c)$ according to Eqn. 2.31 to 2.33. For the conical-shaped tip used in the present experiment, the shape function of the indenter is estimated by the half-angle of the tip, measured by the SEM and assuming a spherical projected area. Once the contact area is determined, the hardness $H$ and the effective Young's modulus, $E_{eff}$ of the material are calculated from Eqn. 2.34 to 2.36.
5.6.1 Nanoindentation of polystyrene tablet using AFM Explorer at 0.1% RH

Surface preparation technique
2.4 cm diameter cross-linked (1%DVB) polystyrene tablet compacted at 1.08 x 10^8 Pa

Experiment reference: PsNa_1

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<td>10.94 Nm^{-1} ± 1.52 Nm^{-1}</td>
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Comments

In this study, 25 indentations of various depths are made on the polystyrene tablet using a cantilever with a spring constant of 10.94 N/m. The nanoindentation tests were conducted at 0.1% RH. Each indentation is made on a different location on the tablet. The maximum contact depth of the indentations, h_{max}, and the maximum load, P_{max} are obtained from the 25 force curves. The results are shown in Figure 5.61. The nanoindentations made on the surface of the polystyrene tablet ranged from a depth of 11.3 nm to 164.5 nm. The load required to indent the surface by 80 nm to 110 nm seemed to vary from 800 nN to 2000 nN depending on the location of the polystyrene tablet. This may be caused by effects of surface roughness or small degrees of tip-blunting.

The hardness of the cross-linked polystyrene and the effective Young's modulus which takes account of the fact that elastic deformation occurs in both the sample and the indenter, are evaluated from the analysis procedure proposed by Oliver and Pharr (1992). The results are presented as Figures 5.62 and 5.63.

From Figure 5.62, the evaluated values of hardness decrease as the contact depth increases. This is an often observed phenomena in nanoindentation studies. This may
be attributed to the fact that the tip encountered defects in the material. Above the contact depths of 60 nm, the value of hardness remained fairly constant at 0.11 GPa ± 0.01 GPa (based on the standard deviation of data points for contact depths greater than 60nm). The evaluated values for the effective Young's modulus of the material also seemed to decrease with increasing contact depth (Figure 5.63) till a depth of 60 nm. A mean value of $E_{\text{eff}}$ may be taken as 1.2 GPa ± 0.3 GPa for contact depths greater than 60 nm.

Figure 5.61 Maximum contact depth of nanoindentations conducted at 0.1% RH versus maximum load
Figure 5.62 Hardness of cross-linked polystyrene at 0.1% RH, evaluated using the Oliver-Pharr procedure, versus contact depth.
Figure 5.63 Effective Young's modulus of cross-linked polystyrene at 0.1% RH, evaluated using the Oliver-Pharr procedure, versus contact depth.
5.6.2 Nanoindentation of polystyrene tablet using AFM Explorer at 65% RH

**Surface preparation technique**

2.4 cm diameter cross-linked (1%DVB) polystyrene tablet compacted at $1.08 \times 10^8$ Pa

**Experiment reference:** PsNa_2

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<td><strong>Calculated spring constant</strong></td>
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**Comments**

Nanoindentation on the surface of the polystyrene tablet has been carried out using a 15.41 N/m cantilever spring at 65% RH. A total of 40 indentations on different locations on the tablet have been made. Information of the maximum contact depth and maximum load are obtained from the 40 force-curves acquired and the results are presented in Figure 5.64. Nanoindentations as small as 2.67 nm were made possible by the high resolution of the AFM Explorer and the sharp probe tip used. The maximum contact depth indented on the surface measures to 217 nm. The scatter in the data points suggests that at different locations on the tablet, an identical indentation depth required different loads.

The hardness, $H$, and the effective Young's modulus, $E_f$, of the cross-linked polystyrene subjected to an RH of 65% are calculated based on the Oliver-Pharr (1992) procedure. The results (Figure 5.65 and 5.66) show a clear trend of decreasing values of hardness and effective Young's modulus as the contact depths are increased. This behaviour is previously observed in PsNa_1. At very small contact depths, the hardness values evaluated are in the region of 65 GPa. This is thought to be unrealistic and the results are therefore omitted from Figure 5.65. As the contact depth increases to 57 nm and above, the evaluated hardness is much more realistic at $0.08$ GPa $\pm$ $0.03$ GPa based on the standard deviation of the data points.
Chapter 5 Results

The calculated values of effective Young's modulus range from 37 GPa at a contact depth of 1.01 nm to 1 GPa at 200 nm. Data points acquired at larger indentation depths are more representative of the material and avoid surface defects. Hence, a mean value of 1 GPa ± 0.477 GPa is calculated for the effective Young's modulus of polystyrene at 65% RH. The results from the nanoindentation tests at low and high RH are compared and discussed in Chapter 7.

Figure 5.64 Maximum contact depth of nanoindentations conducted at 65% RH versus maximum load
Figure 5.65 Hardness of cross-linked polystyrene at 65% RH, evaluated using the Oliver-Pharr procedure, versus contact depth.
Figure 5.66 Effective Young's modulus of cross-linked polystyrene at 65% RH, evaluated using the Oliver-Pharr procedure, versus contact depth.
CHAPTER 6  STATISTICAL ANALYSIS OF RESULTS

6.1 INTRODUCTION

Adhesion measurements are naturally stochastic with variations occurring in measured values for consecutive measurements between the same surfaces, as well as the expected variation that arises due to different contact site topography for the same samples. It is important that a statistical method is employed to enable the discrimination of real trends from random scatter in the data.

Student's t-test (Kreyszig, 1993) was conducted on the experimental results acquired in the adhesion, applied load and contact time studies of polystyrene surfaces to evaluate the confidence interval for the data. The confidence interval simply denotes the upper and lower limits of error associated with the measured value. In estimating the confidence interval for a set of data, the standard deviation of the data from a mean value has to be calculated and the confidence level has to be chosen. The confidence level denotes the probability of getting an interval that will include the unknown exact value of the parameter. For example, a confidence level of 95% means that about 95% of the samples that are obtained will yield confidence intervals that do include the value, whereas the remaining 5% do not.

For all the adhesion, applied load and contact time studies, the t-test procedure was performed on the basis of a 90% confidence level. In order to calculate the confidence interval, the mean value and standard deviation for that particular set of measurements has to be evaluated. The calculated confidence intervals will set the upper and lower limits of a mean value for that particular set of data at the particular relative humidity, applied load or contact time. The sample calculation of the analysis is presented in Appendix 2.
6.2.1 t-test for adsorption and desorption cycle of PsAd_1

Adsorption for a 12 \, \text{um} \, \text{diameter PS particle interacting on PS tablet}

Experiment reference: PsAd_1

Figure 6.1 Student’s t-test analysis results on adsorption for a 12 \, \text{um} \, \text{diameter PS particle interacting on PS tablet (PsAd_1)}

In this investigation, adsorption of moisture was conducted prior to desorption. The Student’s t-test conducted on the adsorption data, taking a mean of 5 individual force curves, shows large confidence intervals especially at 32\% RH and 55\% RH. This indicates that at 32\% RH and 55\% RH, the pull-off forces acquired showed a significant amount of scatter.
Desorption for a 12 µm diameter PS particle interacting on PS tablet

Experiment reference PsAd_1

Figure 6.2 Student’s t-test analysis results on desorption for a 12 µm diameter PS particle interacting on PS tablet (PsAd_1)

The same statistical analysis is performed on the desorption data. In this study, 5 force curves were taken at each relative humidity. From Figure 6.2, large confidence intervals at 35% and 50% RH can be observed which imply large errors associated with adhesion data at these relative humidities.
6.2.2 t-test for adsorption and desorption cycle of PsAd_2

Adsorption for a 12 μm diameter PS particle interacting on PS tablet
Experiment reference PsAd_2

Figure 6.3 Student's t-test analysis results on adsorption for a 12 μm diameter PS particle interacting on PS tablet (PsAd_2)

In this study, desorption of moisture was carried out before adsorption. Three force curves were acquired for each relative humidity. From the Students t-test analysis of the adsorption data, it is obvious that the confidence intervals at relative humidities 2%-60% are rather small, which indicates that the errors associated with the data are not large. At 65% and 70% RH, the errors are considerably larger which indicates a wide spread of experimental data at these conditions.
Desorption for a 12 µm PS particle interacting on PS tablet

Experiment reference PsAd_2

Figure 6.4 Student’s t- test analysis results on desorption for a 12 µm diameter PS particle interacting on PS tablet (PsAd_2)

Three individual force curves were taken at each interval of relative humidity. The large confidence intervals at high humidities were observed in the desorption data, for relative humidities exceeding 55% RH. With hindsight, the scatter in the data in this region can be attributed to the wide range of applied loads at which the force curves were captured or possibly due to multiple contacts, as these data were collected using the custom force instrument. At 55% RH, force curves were captured at applied loads ranging from 2500 nN to 3100 nN. From Figure 5.1 and 5.6, it has been shown that the applied load clearly affects the magnitude of adhesive forces at 60% RH.
6.2.3 t-test for adsorption and desorption cycle of PsAd_3

Adsorption for a 10 μm diameter PS particle interacting on PS tablet

Experiment reference PsAd_3

Figure 6.5 Student’s t-test analysis results on adsorption for a 10 μm diameter PS particle interacting on PS tablet (PsAd_3)

This study was conducted using the AFM Explorer. In all the studies carried using the AFM Explorer, the adsorption cycle was conducted first. Six force curves were taken at each relative humidity. The t-test shows that the confidence intervals for the data are consistently small throughout the whole range of relative humidity from 2% to 65%. The reduced error observed from the small confidence intervals may have been due to the significant reduction of multiple contacts as a smooth region on the tablet was selected from the tablet topographical information acquired. Using the AFM Explorer, the applied load at which force curves were taken could also be controlled more accurately. This might have reduced plastic deformation effects and hence lead to smaller errors in the data. The largest scatter of data was found at lower ranges of relative humidities; at 2%, 10% and 20% RH. At 20% RH, the confidence interval of the data was largest at ±107 nN.
In the desorption cycle, the t-test was performed based on the mean adhesion value calculated from the adhesion values from six force curves at each interval of relative humidity. The computed t-test shows the largest confidence interval for the set of data acquired at 25% RH. As shown in Figure 6.6, the confidence intervals for all the other relative humidities are very small.
6.2.4 t-test for adsorption and desorption cycle of PsAd_4

Adsorption for a 10 μm diameter PS particle interacting on PS tablet

Experiment reference PsAd_4

Figure 6.7 Student’s t-test analysis results on adsorption for a 10 μm diameter PS particle interacting on PS tablet (PsAd_4)

In the adsorption cycle for PsAd_4, the confidence intervals at a confidence level of 90% are consistently low throughout the range of relative humidities. The mean adhesion force was evaluated based on the average of adhesion value of eight individual force curves.

The confidence intervals of the data range from ±20.16 nN at 21% RH to the largest value of ±119 nN at 9.9% RH. This shows that the adhesion values obtained from the eight individual force curves are highly reproducible with little scatter in the data points.
Desorption for a 10 μm diameter PS particle interacting on PS tablet

Experiment reference PsAd_4

Figure 6.8 Student’s t-test analysis results on desorption for a 10 μm diameter PS particle interacting on PS tablet (PsAd_4)

Compared to the adsorption cycle (Figure 6.7), data acquired in the desorption cycle show larger confidence intervals at 15% RH, 35% RH and 55% RH despite the same number of force curves being captured at each interval of relative humidity. At 15.5% RH, the confidence intervals deviated from the mean value by approximately 20%. This indicates a high scatter in the data and one possible explanation is inhomogeneous desorption of moisture caused by surface roughness. At other relative humidities, the errors, as shown by the small confidence intervals are insignificant.
6.2.5 t-test for adsorption and desorption cycle of PsAd_5

Adsorption for a 10 µm diameter PS particle interacting on PS tablet

Experiment reference PsAd_5

Figure 6.9 Student’s t-test analysis results on adsorption for a 10 µm diameter PS particle interacting on PS tablet (PsAd_5)

In the adsorption cycle in PsAd_5 the upper and lower limits of the confidence intervals lie very closely to the mean adhesion values, evaluated from the average adhesion force of eight force curves at each relative humidity. The largest scatter of data occurred at 10% RH and 15% RH. The standard deviations at these relative humidities are 92.6 nN and 91.3 nN respectively. At other relative humidities, the confidence intervals are uniformly small.
In this study, eight force curves were acquired at each interval of relative humidity. The confidence intervals of the data points in the desorption cycle in PsAd_5 range from ±12.9 nN at 31.2% RH to ±194 nN at 15% RH. At humidities of 75% RH to 20% RH, the confidence intervals are small which shows that at these relative humidities, the acquired data points are very reproducible. The confidence intervals are largest at 11.3% RH and 15% RH.
6.2.6 t-test of adsorption and desorption cycles for PsAd_6

Adsorption for a 10 μm diameter PS particle interacting on PS tablet

Experiment reference PsAd_6

Figure 6.11 Student’s t-test analysis results on adsorption for a 10 μm PS diameter particle interacting on PS tablet (PsAd_6)

In this study, the topography of the tablet was not taken prior to force measurements. Despite that, the t-test shows that within a confidence level of 90%, the confidence intervals at 1% RH to 60% RH are not large based on the mean adhesion value of six individual force curves. At higher relative humidities of 55%RH and 60% RH, the scatter in the data is more pronounced. This effect was also observed in the t-test for PsAd_1 and PsAd_2 where the topography of the tablet was not known. This may be due to the fact that when force measurements were taken, the particle was not in contact with a smooth region on the tablet. This was confirmed when the topography of the tablet was measured after the force measurements. Furthermore, at higher relative humidities, there is a greater rate of change of adhesion with RH. This, coupled with the uncertainty associated with surface roughness is likely to be the source of larger confidence intervals.
6.3 t-test of Contact time experiments for a 12 µm PS particle interacting on PS tablet

Figure 6.12 Student's t-test analysis for results of the effect of contact time on the force of adhesion between 12 µm diameter polystyrene particle interacting on a PS tablet at 65% RH.

In the contact time experiments, three separate sets of particles and cantilevers were used for different applied loads. At each time interval, five force curves were acquired consecutively. Even though all the experiments were conducted at 65% RH, the confidence intervals were relatively small. At the applied load of 380 nN, the errors associated with the data points were very small, as shown by the results of the t-test. At 1600 nN, the confidence intervals were marginally higher and at 5000 nN where non-elastic deformation was mostly likely to occur, the confidence intervals were largest when the contact time was 0.5 seconds and 1 second.
6.4 t-test of applied load experiments for a PS particle interacting on PS tablet

Effect of applied load on the force of adhesion between a 12 μm diameter polystyrene particle interacting on a polystyrene substrate with varying relative humidity
Experiment reference: PsAl_2

Figure 6.13 Student’s t-test analysis for results of the effect of applied load on the force of adhesion between a single polystyrene particle interacting on a PS tablet at 1% RH, 35% RH and 65% RH.

The errors associated with the results of PsAl_2 are consistently small throughout the whole range of applied loads from 200 nN to 3500 nN in all three relative humidities. Six force curves were acquired at each interval of applied load at 1% RH, 35% RH and 65% RH. The standard deviation of the mean adhesion forces are also insignificantly small. This shows that the data are very reproducible.
Effect of applied load on the force of adhesion between a 14 μm polystyrene particle interacting on a polystyrene substrate with varying relative humidity
Experiment reference: PsAl_3

Figure 6.14 Student's t-test analysis for results of the effect of applied load on the forces of adhesion between a single polystyrene particle interacting on a PS tablet at 65% RH.

The t-test for PsAl_3 reveals a larger confidence interval compared to PsAl_2. Six force curves were acquired at each interval of applied load in both the ascending and descending applied load experiments. As the applied load was increased from 4000 nN to 31 μN, the confidence interval is approximately ±230 nN. The larger confidence interval may be due to the increasing effects of non-elastic deformation at the contacting surfaces. As the applied load decreases, the measured adhesion forces show less scatter, as confirmed by the smaller confidence intervals.
CHAPTER 7 DISCUSSION

7.1 INTRODUCTION

In this chapter, the results and observations obtained in the experimental studies of polystyrene spheres are discussed. Section 7.2 and Section 7.3 discuss the effect of relative humidity and applied load on the force of adhesion of polystyrene particles respectively. The effect of contact time on the adhesion of polystyrene surfaces at 65% RH is deliberated in Section 7.4. The last section of this chapter is dedicated to the discussion of the implications of experimental results from the nanoindentation studies at 0.1% RH and 65% RH.

7.2 THE EFFECTS OF RELATIVE HUMIDITY ON THE FORCE OF ADHESION

Two investigations were carried out using the custom-built instrument to investigate the effect of relative humidity on adhesive forces for a PS particle interacting on a PS tablet at two different positions on the surface. Both sets of results (Figures 6.1, 6.2, 6.3 and 6.4) clearly indicate a strong dependency on relative humidity, especially at higher humidities, both for adsorption and desorption cycles.

In the first study (Exp. ref. PsAd_1), for the adsorption cycle (Figure 6.1), the force of adhesion at humidities ranging from 1.5% to 55% remained fairly constant at 300-500 nN. A steep increase of the adhesion force to 2000 nN was observed at 60% RH and the results from this humidity onwards also show more scatter. In the desorption cycle (Figure 6.2), the adhesion force was found to be lower at conditions of 75% RH to 60% RH. The peak of adhesion force was observed at 45% RH and then declined sharply to approximately 100 nN at 30% RH and below.

Closer agreement between the adsorption and desorption data was observed in the second series of experiments (Exp. ref. PsAd_2). For this series, the desorption cycle was conducted first and the force of adhesion was found to be significantly higher
Chapter 7 Discussion

compared to the previous study at relative humidities of 75% to 60%. Although the
obtained values in this range of relative humidity were in the 3000 to 4500 nN region,
these values were lower than the predicted value for a perfect wetted system,
described by Eqn. 2.4 when \( \cos \theta \) term becomes unity as \( \theta \rightarrow 0 \). From Eqn. 2.4, the
adhesion force between a particle with a diameter of 12 \( \mu \)m and a flat substrate in the
presence of adsorbed moisture is calculated to be 5500 nN. It is not surprising that the
measured force is lower than this predicted value because in reality, the system is
unlikely to have a contact angle of zero. In fact, values of \( \theta \approx 90^\circ \) have been reported
for polystyrene by Schmitt et al. (1999), which would yield zero adhesion between the
surfaces. However, two data points from the adsorption cycle at 70% RH exceed this
value. Deformation at the particle-substrate interface may increase the contact radius,
hence increasing the effective value of \( R \) in Eqn.2.4. Alternative explanations would
be the contribution from solid-solid van der Waals attractive forces, or the possibility
of multiple liquid bridge contacts.

In both investigations, hysteresis was observed in the solid-solid contact gradient.
This hysteresis effect was absent in the beginning of the adsorption cycle (Figure
5.18, Section 5.4.1). The effect is more apparent at high humidities and although the
extent of the hysteresis decreased as desorption occurred, it was not totally reversible
(compare Figures 5.18 and 5.24 in Section 5.4.1). This may be attributed to slower
rates of desorption compared to adsorption of water, i.e. it is possible that full
equilibrium was not reached on desorption. In a similar system, Mangipudi et al.
(1996) also found adhesion hysteresis for the two polystyrene (PS) films in contact,
where the loading-unloading curves do not superimpose, as would be predicted by
JKR theory for a perfectly elastic system. However, in their study the phenomenon is
repeatable, i.e., the loading and unloading curves for different experimental cycles are
coincidental, (e.g., loading curve for cycle 1 superimposes on loading curve for cycle
2 but the loading -unloading curves for cycle 1 are not coincidental), which indicates
that the hysteresis is not a permanent effect. The authors attributed the adhesion
hysteresis to contact induced rearrangement of the interface that may occur when the
surfaces are in contact under a finite applied load. Unfortunately they did not
investigate the influence of relative humidity.
In the experimental studies conducted using an AFM Explorer, the adhesion forces measured followed a less apparent trend as the relative humidity was ramped up and down compared to the results obtained using the custom-built force instrument. This apparent paradox is most likely explained by the presence of multiple capillary bridges that are an unavoidable feature of working without being able to locate a precise contact site on a single particle using the custom-built instrument. This argument is further supported by the results in Figure 5.57 for the adhesion study conducted using the AFM without prior topographical scanning. A similar increase in adhesion was observed as relative humidities in excess of 60%, suggest that multiple capillary bridges have formed. Scanning after the adhesion study confirmed that contact site to involve at least two particles on the tablet surfaces.

The lack of a notable increase in adhesion at relative humidities above 60% in the AFM adhesion studies is most likely attributable to the lower and more consistent applied loads used in the AFM. The applied load is typically of the order of 1000 nN which is low enough to prevent significant asperity deformation, as discussed in Section 7.3. The small quantity of adsorbed water on the surface may therefore not be sufficient to smother the asperities and form a full capillary bridge.

The hysteresis in the contact region of force curves at high relative humidities previously observed in experimental results obtained from the custom-built instrument is absent in the AFM results. This can be attributed to the difference in the applied load between the contacting polystyrene surfaces. In the force measurements conducted using the AFM, the applied load is kept at a fairly low value of below 1000 nN, which minimises the effects of non-elastic deformation at the contact area.

In Figure 7.1, results of all the adsorption cycles (PsAd_3, PsAd_4, PsAd_5 and PsAd_6) acquired from the AFM are plotted against relative humidity. These results are compared to PsAd_1 and PsAd_2 obtained from the custom-built instrument. The adhesion forces are scaled by dividing the adhesion forces by the particle diameter used, as the particle size used in the studies varied slightly. This is necessary to facilitate a direct comparison of the adhesion forces as the magnitude of adhesion forces is dependent on particle size. From this figure, it is evident that apart from
PsAd_6, adhesional values acquired from the AFM are consistently higher than results obtained from the custom built instrument across the range of relative humidities from 2% RH to 50% RH. This is undoubtedly due to the ability to locate smooth regions on the tablet for force measurements using non-contact scanning on the AFM, therefore reducing the probability of multiple asperity and multiple particle contacts.

Figure 7.1 Comparison of adhesion forces from adsorption data acquired from the AFM and custom-built instrument

Contact mechanics theories for elastic contacts such as JKR and DMT are used to compare the predicted and measured values of adhesion forces. In order to calculate the pull-off forces using these theories, a published value of 0.04 J/m² (Rimai et al 1993) is used for the surface energy of polystyrene. The equations proposed by Johnson et al. (1971) for the JKR model and by Derjaguin et al. (1975) for the DMT model are detailed in Section 2.5.1 and 2.5.2 respectively. Eqn. 2.19 was used to calculate the pull-off forces using the JKR model and Eqn. 2.20 was used for the DMT model.
Figure 7.2 Comparison of predicted and measured adhesion forces of a 12 μm polystyrene particle interacting with a polystyrene substrate using the custom-built instrument.

Figure 7.2 shows that the discrepancy between the predicted values of adhesion forces by both JKR and DMT theories and the measured values from PsAd_1 and PsAd_2 are large. The contrasting value of adhesion forces may be attributed to several factors. Both PsAd_1 and PsAd_2 are conducted using the custom-built instrument, which is unable to provide topographical information on the polystyrene substrate. Hence, the contact geometry between the particle and substrate is unknown. Secondly, effects of surface roughness are not included in either the JKR or DMT contact mechanics theories. To verify this point, the measured pull-off forces are substituted into equations 2.19 and 2.20 and the resulting particle diameters predicted by the JKR and DMT theories are calculated respectively. Bearing in mind that both the JKR and DMT theories are only expected to be valid at low relative humidities, (i.e. no capillary bridging) a mean value of adhesion force of 650 nN is used. The JKR theory yields a particle with a diameter of 3.44 μm while the DMT theory yields a particle diameter of 2.59 μm. From this simple analysis, it is shown the effective particle diameter is significantly lower than the actual value. This difference is undoubtedly
due to the effect of surface roughness i.e. effective contact area reduction due to contact between asperities.

The comparison between the predicted values of pull-off forces by JKR and DMT is further extended to experimental results obtained from the AFM Explorer. This is shown in Figure 7.3.

Figure 7.3 Comparison of predicted and measured adhesion forces of a 10 μm diameter polystyrene particle interacting with a polystyrene substrate using the AFM Explorer

The results obtained from the AFM Explorer are in much better agreement with the predicted pull-off forces from JKR theory. This is hardly surprising, as the contact geometry of the substrate is known through the topographical information obtained by the AFM enabling contact on relatively smooth, single particle surfaces. Furthermore, the applied load in these experimental studies was also better controlled. It is clear from Figures 7.2 and 7.3 that the JKR theory is in closer agreement with the current experimental results. This observation is in agreement with the comments of Muller (1980) who predicted that the JKR theory is more applicable to materials that are adhesive with low values of elastic moduli compared with the DMT theory.
7.3 THE EFFECT OF APPLIED LOAD

Using the custom-built instrument, an experimental study was conducted on the influence of applied load on the measured force of adhesion between polystyrene surfaces for three separate humidities; 14%, 30% and 60% RH. The adhesion force between a 12 µm polystyrene particle and a polystyrene compact was measured with increasing applied load at these three different relative humidities, as described in Section 5.3. The objective of this study is to investigate the effect the applied load has on the adhesion forces for better understanding of the behaviour of the interacting surfaces. The results of this investigation are shown in Figure 5.1.

At 14% RH, the applied load was increased from 500 nN to 6500 nN. A total of 12 force curves were taken over this range of applied load. The force of adhesion measured varies from 100 nN to 500 nN. The influence of applied load has no apparent effect on the measured adhesion forces at this relative humidity as shown in Figure 5.1.

Using the same polystyrene particle on exactly the same position on the compact, the relative humidity was increased to 30% RH. The measured force of adhesion showed no dependency on the increase of applied load from 360 nN to 5500 nN. The adhesion forces measured in this range of applied loads were consistently around 100 to 500 nN, as for the data collected at 14% RH.

The results at 14% RH and 30% RH indicate that applied load has little influence over the measured forces of adhesion. This conclusion is further corroborated by results obtained for the polystyrene system in the adhesion studies, shown in Figures 5.16, 5.25, 5.26 and 5.27. At relative humidities below 55% RH, there was little scatter in the data, with a typical confidence interval of ±200 nN although the applied load was varied for each force curve taken.

The influence of applied load on the adhesion force between polystyrene surfaces was significantly greater when the relative humidity was increased to 60%. The results as
shown in Figure 5.1, indicate that the force of adhesion increased linearly from 1250 nN to 2250 nN as the applied load was increased from 1000 nN to 5000 nN.

At high applied loads of above 1000 nN, the force curves obtained in the 14% RH and 30% RH systems showed slight hysteresis in the contact region, whereby the approach and withdrawal curves do not superimpose. This effect was absent at lower applied loads, which suggests that at high applied loads, the polystyrene particle and the polystyrene compact were exhibiting plastic behaviour. However, the plasticity was not sufficient to provide a detectable increase in adhesion at these relative humidities. At 65% RH and high load, the hysteresis in the contact region is more notable, which is consistent with the observed increased in adhesion with applied load.

An identical investigation of the effect of applied load and relative humidity on the force of adhesion between polystyrene surfaces was carried out using the AFM Explorer. As before, the investigation was carried out at three relative humidities; 1% RH, 35% RH and 65% RH. For each relative humidity, the same 12 µm polystyrene particle was mounted on the back of a 16 N/m cantilever and the same contact site was used. The applied load was increased from approximately 200 nN to 4000 nN. The results of this investigation are shown in Figure 5.6.

At 1% RH and 35% RH, the adhesion forces measured were not hugely affected by the increasing applied load, although at 1% RH, the forces increased from 480 nN at an applied of 200 nN to 1000 nN at an applied load of 3800 nN. This increase in adhesion forces at low relative humidity may be due to the crushing of small surface asperities of both the polystyrene particle and substrate. It is interesting that the adhesion at 35% RH is significantly higher that at 1% RH. Given the high level of confidence in duplicating the contact site, this increase in most likely explained by the difference in relative humidity between the extremely dry state at 1% and 35% and the associated levels of adsorbed water.

At 35% RH, the adhesion was observed to be constant with applied load. Presumably this majority of asperity deformation had previously occurred in the test at 1% Rh, leaving the contact to be essentially elastic.
At 65% RH, the adhesion forces remained fairly constant at 2200 nN from the range applied loads of 200 nN to 1000 nN. From an applied load of 1000 nN up to 2500 nN, a transition appeared where the measured adhesion forces increase gradually to 3200 nN. Force curves obtained at 65% RH at high loads also showed a significant increase in hysteresis in the contact region. The transition region at 1000 nN for this relative humidity is further evidence to suggest the onset of plastic deformation of the contacting surfaces.

This hypothesis was tested using contact mechanics theories which describe both plastic and elastic behaviour. The comparison between measured adhesion forces and predicted pull-off forces in the previous section indicates that the JKR theory is in better agreement with the current data. Hence, the JKR theory will be used to calculate the contact area of the surfaces under load if the surfaces were behaving elastically according to Eqn. 2.14 (reproduced below). The computed contact areas will then be coupled with a published value of the yield stress of cross-linked polystyrene to predict the applied load at which this yield point occurs. The same analysis is also conducted using the Maugis-Pollock (MP) contact mechanics theory, which accounts for adhesion-induced plastic deformation between the contacting surfaces. The authors proposed that for plastic deformation resulting from the combination of stresses due to the surface forces of a sphere interacting on a flat and the applied load, the contact radius is related to the applied load and the work of adhesion by Eqn. 2.23 (reproduced below).

\[ JKR \quad a^3 = \frac{R}{K} \left[ P + 3w_a \pi R + \left[ 6w_a \pi RP + \left( 3w_a \pi R \right)^2 \right]^{1/2} \right] \quad Eqn \ (2.14) \]

\[ MP \quad a^2 = \frac{1}{\pi H} \left( P + 2w_a R \right) \quad Eqn \ (2.23) \]

where \( a \) is the contact radius, \( R \) is the radius of the particle, \( w_a \) is the thermodynamic work of adhesion, \( P \) represents an externally applied load, \( H \) is the hardness of the material and \( K \) is given by
\[
\frac{1}{K} = \frac{3}{4} \left[ \frac{(1-\nu_1^2)}{E_1} + \frac{(1-\nu_2^2)}{E_2} \right]
\]

Eqn. (2.16)

where \(E_1\) and \(E_2\) and \(\nu_1\) and \(\nu_2\) are the Young’s modulus and Poisson’s ratio of the two interacting material respectively.

The mechanical properties for cross-linked polystyrene used are published values by Rimai et al. (1994). The surface energy for cross-linked polystyrene is taken to be 0.04 J/m², hardness is 32.4 GPa, Poisson’s ratio is 0.38, Young’s modulus is 2.55 GPa and yield stress is 10.8 MPa. For a particle diameter of 12 µm, \(R = 6 \mu m\), \(w_d = 2\gamma = 0.08 \text{ J/m}^2\) and \(K = 1.9869 \times 10^9\). In order to evaluate the load at which the yield stress of 10.8 MPa is reached, the contact radius is evaluated according to Eqn. 2.14 as follows. For each experimental value of applied load, the JKR Eqn. 2.14 is used to predict a value of the contact radius and hence the contact area. These values are combined with the experimental applied loads to give a range of estimated contact stresses. The applied load and contact area dimensions corresponding to the yield stress can then be found.

According to Eqn. 2.14, the yield stress is reached at an applied load of \(P = 2825 \text{ nN}\), with a contact radius of 299 nm. Assuming a circular contact region between the particle and the substrate, the contact area is then 0.28 µm². Conducting the same analysis using the MP model using Eqn. 2.23, the yield point occurs at an applied load of 1508 nN with a calculated contact area of 0.14 µm².

The loads at which the yield stress is predicted to be exceeded, are shown on the plot of adhesive force versus applied load in Figure 7.4. The prediction of adhesion from the JKR theory is also included in this figure.
Results of the analysis of the yield point reveal that the load required for the initiation of plastic deformation using the JKR theory is significantly higher compared to the MP theory. According to the JKR theory, yielding of the surfaces occurs at an applied load of 2825 nN with a calculated contact area of 0.28 µm² compared to the MP theory which predicts the yield point at an applied load 1508 nN with a calculated contact area of 0.14 µm². It is significant that the onset of plastic deformation as predicted by MP coincides closely with the transition observed in the experimental results. This gives support to the argument that plastic deformation is occurring at the contact surfaces at high humidities. The prediction of load at which the yield stress is exceeded by the JKR model is unrealistically high.

The comparison of the measured adhesion forces to the predicted pull-off forces by the JKR theory for elastic behaviour shows an excellent agreement up to an applied load 1300 nN. This analysis shows that the interaction between the polystyrene surfaces at high humidities behaves elastically up to an applied load of 1300 nN. and
above this value plastic deformation is occurring at the contacting surfaces due to the yielding and softening of the material caused by moisture sorption.

This hypothesis was further verified when a second investigation into the effect of applied load at high humidities on the force of adhesion was conducted. This study (PsAl_3) was carried out at a relative humidity of 65% RH using a 12 μm polystyrene particle mounted on a stiff cantilever with a spring constant of 67 N/m. The range of applied loads of 4 μN to 31 μN is much higher compared to the previous two studies. Force curves were initially captured in the order of increasing load and using the same particle on the same position on the polystyrene tablet, force curves were then acquired in the order of decreasing load (Figure 5.11). The measured adhesion forces increased gradually from 2000 nN to 3400 nN as the applied load was increased from 4 μN to 31 μN. When the adhesion forces were measured in descending order of applied load, the magnitude of these forces was significantly higher compared to the results from the ascending order of applied load. This indicates that the contacting surfaces have already deformed plastically during the increase in applied load, and a larger contact area has formed between the surfaces. Hence, any further contact at applied loads above that corresponding to the yield stress will yield larger adhesional forces due to this increase in contact area even though the load may be decreasing. In addition, further deformation of the surfaces will occur even when decreasing the applied load because the load required for yielding is still much lower than the load inflicted on the surfaces.

On decreasing the applied load, a constant value of adhesion is reached at about 13 μN. We can assume from the evidence that above this load, the contact area is undergoing plastic deformation, and below this load, the extent of plastic deformation is sufficient to reduce the contact stress to a value lower than the material yield stress.
7.4 THE EFFECT OF CONTACT TIME ON ADHESION

In order to investigate further the interaction of polystyrene surfaces at high applied loads and high relative humidities, a study of the effect of contact time was initiated using the AFM Explorer. The study consisted of three individual sets of experiments conducted at three different applied loads of 380 nN, 1500 nN and 5000 nN. A different polystyrene particle and cantilever spring was used for each of these experiments to minimise errors on the measured adhesion forces. The relative humidity was kept at 65% RH in all the experiments. The contact time was increased from 200 microseconds to 10 seconds using small increments, and at each time interval, 5 force curves were captured.

The results of this study are presented in Figure 5.58. The adhesion forces measured were scaled with the diameter of the polystyrene particle because the size of particles used varied slightly in each set of experiments. At low and medium loads, the increase in contact time did not seem to affect the measured adhesion forces. The only exception was observed at an applied load of 380 nN, when the measured forces increased from 690 nN at 0.01 seconds to 1264 nN at 0.1 seconds. As the contact time was further increased to 10 seconds, the adhesion forces remained virtually constant at 1256 nN. At an applied load 1500 nN, the adhesion forces between the polystyrene surfaces were not influenced by the increase in contact time. The forces remained at approximately 1100 nN throughout the increase in contact time.

As the applied load was increased to 5000 nN, a significant increase in adhesion forces could be observed as the contact time rose from 0.1 seconds. The forces measured increased from 1501 nN for a contact duration of 0.1 seconds, to 2442 nN at 1 second. This time-dependency of adhesion forces at high loads and high humidities suggests that visco-elastic or visco-plastic effects may be a contributing factor to the increase in the adhesion forces. A similar study on the visco-elastic behaviour of polystyrene particles has been previously published by Reitsma et al. (2000). The authors measured the pull-off forces of a 27.2 μm diameter polystyrene sphere interacting with a flat silica substrate with varying loading rates using a Nanoscope III AFM. Their results show that as the loading time increases above 1 second, the pull-
off forces also increase. It is difficult to draw direct comparisons of the published work with the present results as the absolute contact time between the surfaces was not cited in the paper. However it is worth noting that upon imaging the polystyrene bead using electron microscopy, Reitsma et al. (2000) concluded that the observed time-dependent behaviour was due to surface asperities undergoing large plastic deformations in the contact zone.

The results from the current work clearly indicate a transition of behaviour in the polystyrene surfaces studied from being linearly elastic at low relative humidities and low loads to being plastic at high relative humidities and high loads. Evidence from the literature supports this hypothesis. Schaefer et al. (1994) measured the pull-off force as a function of the applied load for a 5 μm and a 7 μm diameter cross-linked polystyrene sphere. The results for the 5 μm polystyrene sphere indicated a slight increase of pull-off force with increasing loading force. The authors attributed the non-linearity of the results to viscoelastic or an inelastic response of the particles to the loads. This hypothesis was also further strengthened when the authors observed an hysteretic effect; i.e. the loading and unloading force curves at the contact region do not superimpose on each other. The authors analyzed the loading and unloading region of the force vs. distance curve to account for the particle deformation. This was determined by subtracting the controlled motion of the substrate from the responding motion of the cantilever. If the particle and the substrate were infinitely hard, the two motions would be coincident. The sphere deformation during loading was found to follow a linear behaviour with the loading force. Under the maximum load of 50 nN, the sphere deformed by 50 nm. Studies on the effect of applied load on the force of adhesion for the 7 μm polystyrene particle showed a slightly less pronounced influence.

In a later study, Schaefer et al. (1995) studied the effect of applied load for a 8 μm diameter cross-linked polystyrene sphere interacting with a graphite substrate under ambient conditions. The pull-off forces were found to be constant for the range of loading between 40-410 nN. Although Schaefer et al.'s results concur with the present study at lower humidities of 14%RH and 30%RH, the applied stresses subjected on the polystyrene particle interacting with the polystyrene tablet are considerably higher.
in the present investigation. The relative humidity in Schaefer et al.'s experiments was also unspecified in their paper, though under ambient conditions, one can assume that the relative humidity is well below 50%.

Further evidence on the non-elastic behaviour of polystyrene particles could be found in Rimai et al.'s (1990) paper. The authors measured the radius of the contact zone, resulting from the attraction due to surface forces, between spherical polystyrene particles and a silicon substrate, ranging from 2 to 12 μm in diameter using a SEM. The micrographs obtained showed an apparent flat zone at the particle-substrate interface. The flattening-effect was thought to be due to the deformation of the polystyrene spheres rather than the more rigid silicon. The authors also reported that the contact radius varied with the square root of the particle radius which concurs with the contact mechanics model proposed by Maugis and Pollock (1984) (MP) which allows for plastic deformation to occur. Their findings are inconsistent with the 2/3 dependence predicted by models such as the JKR or DMT which only assumes an elastic response between the surfaces. Using the MP model, the estimated work of adhesion was also in good agreement with the surface energies of the materials. Substituting the same value of work of adhesion into the JKR model underestimates the contact radius by 67%. Rimai et al. (1990) concluded that surface forces between the materials can create stresses which exceed their elastic limits and caused plastic deformation to occur.

7.5 NANOINDENTATION STUDIES ON POLYSTYRENE

The nanoindentation technique, so called because of its high resolution in measuring forces and displacements in the nano-scale, has been used to measure directly the mechanical properties of the cross-linked polystyrene used in the present study. More importantly, the effect of relative humidity on the mechanical properties of the polystyrene have been directly evaluated using this technique.

In nanoindentation, the polystyrene surface is probed with a sharp tip using very small loads. Using the Point-Spectroscopy function in the AFM, a continuous recording of the load and penetration depth during a complete cycle of loading and unloading of an
indenter is acquired. The hardness and Young's modulus of the sample studied can then be inferred from this information using well established methods. For the nanoindentation tests in this work, the method of Oliver and Pharr (1992) was used to analyse the nanoindentation data presented in this work. A description of this method is given in Section 2.6.

As mentioned previously, the nanoindentation studies are to facilitate the measurement of the mechanical properties of polystyrene and to study the effect of relative humidity on these properties. Hence, two experiments were conducted at 0.1% RH and 65% RH respectively.

Results of the nanoindentation tests at 0.1% RH are shown in Figures 5.61 to 5.63 in Section 5.6. A wide range of maximum indentation depths were made on the surface, from 15 nm to 140 nm. The contact depths of these indentations are then calculated using the method detailed in Section 2.6.2. The hardness of the material was found to decrease with increasing contact depth. This has been previously observed by a number of investigators and is attributed to the fact that the tip encounters defects in the material with increasing indentation depth. However, for contact depths of 60 nm and above, the hardness remained fairly constant at a mean value of 0.11 GPa with a standard deviation of 0.01 GPa. At these indentation depths, the hardness value is thought to be most representative of the true value as surface effects and the poor resolution of the tip area function are diminished.

The effective Young's modulus, $E_{eff}$ of the polystyrene sample at 0.1% RH was found to follow the same trend as the graph of hardness versus contact depth; decreasing $E_{eff}$ with increasing contact depth. At contact depths of 60 nm to 80 nm, the value of effective Young's modulus hovered around the 1.2 GPa mark. These values of Young's modulus are lower than the published value (Rimai et al., 1993) of 2.55 GPa. It is not surprising that differences arise because the published value of Young's modulus in Rimai et al.'s paper was measured using a bulk polystyrene sample and a tensile tester, whereas in this study, the measurements are performed in the nanoscale.
The nanoindentation studies were then performed on a polystyrene tablet subjected to a relative humidity of 65% RH for 24 hours. Forty individual indentations were made on the surface at various locations. The results of this study are presented in Section 5.6.2. The maximum indentation depths cover a wide range from 2 nm to 217 nm. When the evaluated hardness is plotted against the contact depths, the trend of decreasing hardness with increasing contact depth is observed once again. The values of hardness obtained at low contact depths of <10 nm are unrealistically high and can be dismissed as they are unreliable due to the poor resolution of the tip contact geometry at such small penetration depths. Hence, the data from Figure 5.65 are replotted in Figure 7.5 omitting values from low contact depths.

Figure 7.5 Hardness of cross-linked polystyrene at 65% RH versus contact depths

![Graph showing hardness vs. contact depth](image)

From the figure above, it is much more evident that as the contact depth increases beyond 500 nm and above, the evaluated hardness of polystyrene falls to a mean value of 0.08 GPa with a standard deviation of 0.03 GPa.

Comparing the mean values of hardness of 0.11 GPa at 0.1% RH and 0.08 GPa at 65% RH, the evidence suggests that adsorption of water resulted in a 27% decrease in
hardness of the material. This finding is intuitively explained by the generally
accepted mechanism of amorphous polymer dilution by an adsorbate such as water.
The water molecules diffuse into the surface layer causing swelling and increased
ductility. This phenomenon is reported by Roos (1995) for example.

The effect of relative humidity on the mechanical properties of polystyrene is further
confirmed when the effective Young's modulus of the material is plotted against
contact depth in Figures 5.63 and 5.66. At 65% RH, the values of effective Young's
modulus for contact depths exceeding 50 nm are essentially constant with a mean
value of 1 GPa and a standard deviation of 0.477 GPa. Values of Young's modulus at
smaller contact depths can be neglected for the purposes of this study for reasons
outlined above. Figure 5.63 shows that a value of Young's modulus at 0.1% RH also
falls to essentially a constant value above indentation depths of 50 nm, with a mean
value of 1.2 GPa and a standard deviation of 0.3 GPa.

At 65% RH, the effective Young's modulus of polystyrene has decreased by 17%,
compared to the values at 0.1% RH. From these nanoindentation studies, it is evident
that the adsorbed moisture on the polystyrene surfaces as a result of increased relative
humidity is sufficient to render the surfaces more compliant, both in terms of reduced
hardness and reduced Young's modulus.

In Section 7.3, the effect of applied load and relative humidity on the adhesion forces
of interacting polystyrene surfaces were analysed using well-established contact
mechanics models to evaluate the point at which yield is reached. The mechanical
properties of polystyrene used in these models were obtained from published
values by Rimai et al. (1994). However, with the nanoindentation studies, the
measured mechanical properties of polystyrene at 0.1% RH and 65% RH can now be
substituted into the contact mechanics models and used in the analysis of yield point
in the applied load studies. In order to access the load at which yield is reached at both
0.1% RH and 65% RH, the contact areas between the particle and substrate have to be
calculated using Equations 2.14 and 2.23 in accordance with the JKR and MP contact
mechanics theories. The mechanical properties measured from nanoindentation tests
and the loads required to reach the yield stress of 10.8 MPa according to the JKR and MP theories are tabulated as below.

Table 7.1 Mechanical properties of cross-linked polystyrene evaluated by nanoindentation studies

<table>
<thead>
<tr>
<th>Relative humidity</th>
<th>0.1% RH</th>
<th>65% RH</th>
<th>Published value(^1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hardness</td>
<td>0.11 GPa</td>
<td>0.08 GPa</td>
<td>0.0324</td>
</tr>
<tr>
<td>Effective Young's modulus</td>
<td>1.2 GPa</td>
<td>1 GPa</td>
<td>2.55 GPa</td>
</tr>
<tr>
<td>Load (JKR)</td>
<td>10200 nN</td>
<td>12500 nN</td>
<td>2825</td>
</tr>
<tr>
<td>Contact area (JKR) (\mu m^2)</td>
<td>0.936(^2)</td>
<td>1.15</td>
<td>0.28(\mu m^2)</td>
</tr>
<tr>
<td>Load (MP)</td>
<td>330 nN</td>
<td>470 nN</td>
<td>1508.16 nN</td>
</tr>
<tr>
<td>Contact area (MP) (\mu m^2)</td>
<td>0.03 (\mu m^2)</td>
<td>0.044 (\mu m^2)</td>
<td>0.139 (\mu m^2)</td>
</tr>
</tbody>
</table>

The results tabulated above show that at 65% RH, the effective Young's modulus is reduced by 0.2 GPa, or 17% compared to the evaluated value of 1 GPa at 0.1% RH. Therefore, one would expect that a smaller load would be required to reach the yield point according to the JKR theory using the mechanical properties at 65% RH provided that the contact area remained constant. However, the contact area increases with RH, from 0.03 \(\mu m^2\) to 0.044 \(\mu m^2\) and therefore, a higher load is required to reach the yield point (yield stress = Load/Area). In the MP analysis, the hardness value is directly substituted into Eqn. 2.23. It is clear from comparing the applied loads required to reach the yield stress in Table 7.1, that the value based on the JKR model is excessively large. Conversely, the value of applied load based on the MP model is somewhat lower than the load of 1000-1200 nN at which a transition in behaviour occurs.

\(^1\)Rimai et al. (1994)
The effect of pile-up and sink-in was also investigated in the current nanoindentation studies (see Section 2.6.4). According to Bolshakov et al. (1996, 1998), the ratio of \( h_f/h_{\text{max}} \) is indicative of the expected indentation behaviour of a given material. The natural limits for the ratio of \( h_f/h_{\text{max}} \) are between 0 and 1, whereby the lower limit corresponds to fully elastic deformation of the material and the upper limit corresponds to rigid-plastic behaviour.

Bolshakov et al. showed that the amount of pile-up is large only when \( h_f/h_{\text{max}} \) is close to the value of 1 and the amount of work-hardening is small. When \( h_f/h_{\text{max}} \) is less than 0.7, very little pile-up is found no matter what the work-hardening behaviour of the material is. They commented that when \( h_f/h_{\text{max}} \) is larger than 0.7, the accuracy of the Oliver-Pharr method depends on the amount of work-hardening in the material.

Pharr (1998) also remarked upon the effect of pile-up on the estimation of the effective Young's modulus. According to him, when pile-up is significant, the effective Young's modulus may be largely overestimated. When \( h_f/h_{\text{max}} \) is larger than 0.7, the effective modulus is overestimated by 10-16%, presumably by the inadequacy of elastic solutions intrinsic in the Oliver-Pharr method in describing plastic behaviour of materials.

The ratio of \( h_f/h_{\text{max}} \) was calculated for nanoindentation tests at 0.1% RH and 65% RH. The results show that 60% of the nanoindentation results obtained at 0.1% RH have a \( h_f/h_{\text{max}} \) greater than 0.7. At 65% RH, 17 out of the 40 nanoindentation curves have a \( h_f/h_{\text{max}} \) ratio of 0.7 and above. This indicates that independent of relative humidity, the effect of pile-up on the polystyrene surface seemed to be significant. As stated by both Bolshakov and Pharr, this will have a direct impact on the evaluated hardness and effective Young's modulus. The amount of work-hardening of the polystyrene surfaces cannot be directly obtained from the nanoindentation studies but from the apparent effect of applied load on the adhesion forces of the surfaces (Section 7.2), one may infer that the contact area may be described as elastically-plastic in nature. Using finite element analysis, Bolshakov showed that if the material is elastically-perfectly plastic, the Oliver-Pharr method underestimated the contact area by as much as 50%. Taking this into account, the contact areas, hardness and
effective Young's modulus values for cross-linked polystyrene are re-evaluated by increasing the contact areas by 50% as suggested by Bolshakov (1998). The results are shown as Table 7.2 and 7.3.

Table 7.2 The effects of pile-up on the evaluated hardness and effective Young's modulus at 0.1% RH

<table>
<thead>
<tr>
<th></th>
<th>Hardness (GPa)</th>
<th>Effective Young's modulus (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Without pile-up</td>
<td>0.11</td>
<td>1.2</td>
</tr>
<tr>
<td>With pile-up</td>
<td>0.05</td>
<td>0.8</td>
</tr>
</tbody>
</table>

Table 7.3 The effects of pile-up on the evaluated hardness and effective Young's modulus at 65% RH

<table>
<thead>
<tr>
<th></th>
<th>Hardness (GPa)</th>
<th>Effective Young's modulus (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Without pile-up</td>
<td>0.08</td>
<td>1.0</td>
</tr>
<tr>
<td>With pile-up</td>
<td>0.04</td>
<td>0.75</td>
</tr>
</tbody>
</table>

Tables 7.2 and 7.3 show that incorporating the effects of pile-up, the evaluated hardness of cross-linked polystyrene at 0.1% RH is reduced by 54.5% and the evaluated Young's modulus is reduced by 33.3%. The reduced value for hardness at 0.1% RH is in much better agreement with the published value of 0.03 GPa. However, the evaluated effective Young's modulus is still much lower than the published value of 2.55 GPa. At 65% RH, the effect of pile-up has resulted in to a reduction of 50% in the evaluated hardness and a 25% reduction in the evaluated Young's modulus.

The parameters of hardness and effective Young's modulus modified to account for pile-up can be used to predict the applied load required to meet the yield stress, as previously shown in Table 7.1. The results of this exercise are shown in Table 7.4.
Table 7.4 The effects of pile-up on the evaluated hardness, effective Young's modulus and load required for yield at 0.1% RH and 65% RH.

<table>
<thead>
<tr>
<th>Relative humidity</th>
<th>0.1% RH</th>
<th>65% RH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hardness</td>
<td>0.05 GPa</td>
<td>0.04 GPa</td>
</tr>
<tr>
<td>Effective Young's modulus</td>
<td>0.8 GPa</td>
<td>0.75 GPa</td>
</tr>
<tr>
<td>Load (JKR)</td>
<td>16000 nN</td>
<td>17000 nN</td>
</tr>
<tr>
<td>Contact area (JKR)</td>
<td>1.47 μm²</td>
<td>1.58 μm²</td>
</tr>
<tr>
<td>Load (MP)</td>
<td>830 nN</td>
<td>1030 nN</td>
</tr>
<tr>
<td>Contact area (MP)</td>
<td>0.0245 μm²</td>
<td>0.101 μm²</td>
</tr>
</tbody>
</table>

It is interesting to see that when allowing this pile-up, the predicted load for plastic deformation using the MP model is 1030 nN. This agrees closely with the experimental value of applied load at which plastic behaviour occurs in Figure 7.4.

From the nanindentation results, it is evident that the relative humidity has a significant effect on the mechanical properties of cross-linked polystyrene, which directly affects the adhesional properties of the material. The change in the mechanical properties of polystyrene at high humidities shown by this analysis corresponds to the observed elasto-plastic behaviour of polystyrene from both the adhesion and applied load studies.

There are a number of disadvantages to using the AFM for nanoindentation. For instance, the effective strain rate of the indentation process varies as the cross-section of the tip progresses into the sample. This can lead to error for materials where deformation behaviour is strain-rate dependent. Furthermore, the pivoting action of the cantilever implies that the vertical axis of the probe tip will change as it enters the sample, creating a larger area of indentation than otherwise expected. In spite of these shortcomings, the AFM seems to be an ideal instrument for obtaining at least a relative comparison of hardness and Young's modulus measurement, especially given its capability for coupling nanoindentation with surface imaging.
CHAPTER 8  CONCLUSIONS & FUTURE WORK

8.1 STATEMENT OF ORIGINAL PROBLEM

The interaction between a single polystyrene particle and a polystyrene substrate has been previously reported by a number of investigators. However, the effects of relative humidity, applied load and contact time on the adhesion of polystyrene surfaces have not been investigated and these effects are not well understood. It is the primary aim of the current work to characterise the effect of the aforementioned parameters on the adhesion of polystyrene surfaces using high-resolution atomic force microscopy techniques.

It is evident from published literature that the behaviour of polystyrene surfaces cannot be aptly described by elastic contact mechanics models such as JKR and DMT due to non-elastic deformation at the contact area. In the current work, the Maugis-Pollock (MP) model which incorporates elasto-plastic and plastic deformation is used to predict the contact area. When coupled with the published value of yield stress for polystyrene, the applied load at which yield occurs is reasonably predicted at low and high relative humidities.

The mechanical properties of materials are often measured using bulk samples and macro-scale instrumentation, which does not allow detection of important effects at the nano-scale. In the current work, the mechanical properties of cross-linked polystyrene are measured directly using AFM nanoindentation which is capable of characterising the hardness and Young's modulus of the material in nano-scale. The effect of relative humidity on the mechanical properties of cross-linked polystyrene is also investigated.

8.2 PRIMARY CONCLUSIONS

The adhesion forces of a single polystyrene particle, ranging from 10-14 \( \mu \)m in diameter, and a polystyrene substrate has been measured at various relative humidities. From the work conducted using the custom-built instrument, the
dependency of adhesion forces on the relative humidity is greatest at relative humidities of 60% and above. The sharp rise in adhesion above 60% RH can be attributed to the formation of capillary bridges. On occasions, the adhesion exceeded that predicted by Laplace-Kelvin theory suggesting that there was a contribution to adhesion from the solid-solid interaction, and from multiple capillary contacts. In both the experimental studies carried out, hysteresis was observed in the solid-solid contact gradient which suggests non-elastic behaviour at the contact area of the surfaces.

In the experimental studies conducted using an AFM Explorer, the topography of the polystyrene surface was mapped before and after experimental studies which enables the location of the force measurements to be pin-pointed. The effect of relative humidity on the adhesion forces of polystyrene surfaces was less apparent. However, it was observed that adhesional values acquired from the AFM are consistently higher than results obtained from the custom built instrument across the range of relative humidities from 2% RH to 50% RH. This is due to the ability to select smooth, single particle contact sites, compared to the measurements carried out in the custom-built instrument.

When the measured adhesional forces were compared to contact mechanics theories, the theoretically predicted values of adhesion forces by both JKR and DMT theories were found to be much larger than the measured values. This was attributed to the fact that effects of surface roughness are not taken into account in either the JKR or DMT contact mechanics theories. The results obtained from the AFM Explorer are in much better agreement with the predicted pull-off forces from JKR theory.

Using the custom-built instrument, the effect of applied load on the adhesion force between a polystyrene particle and a polystyrene substrate was studied at three humidities; 14%, 30% and 60% RH. The increasing applied load had little effect on the measured adhesion forces at 14% and 30% RH but at 60% RH, the adhesion forces between the polystyrene surfaces were found to be significantly greater as the applied load was increased. This suggests that at high relative humidities and high applied loads, the polystyrene particle and the polystyrene compact were exhibiting non-elastic behaviour.
The effect of applied load and relative humidity on the force of adhesion between polystyrene surfaces was further investigated using the AFM Explorer at three relative humidities; 1% RH, 35% RH and 65% RH. At 1% RH and 35% RH, the adhesion forces measured were not hugely affected by the increasing applied load although at 1% RH, the forces increased from 480 nN at an applied of 200 nN to 1000 nN at an applied load of 3800 nN. This increase in adhesion force at low relative humidity may be due to the crushing of surface asperities of both the polystyrene particle and substrate. At 65% RH, there seemed to be a transition where the measured adhesion forces increased gradually from 2000 nN to 3200 nN as the applied load increased from 1200 nN to 3400 nN. Force curves obtained at 65% RH at high loads also showed a significant increase in hysteresis in the contact regions. The transition region at 1200 nN for this relative humidity is evidence to suggest the onset of non-elastic deformation at the contacting surfaces.

When experimental results from the applied load studies were analysed using JKR and MP theories, the yield point, which denotes the load required for the initiation of plastic deformation, is evaluated. According to the JKR theory, yielding of the surfaces occurs at an applied load of 2825 nN compared to the MP theory which predicts the yield point at an applied load 1508 nN. It is worth noting that the yield point denotes the initiation of fully plastic deformation of the surfaces, therefore the initiation of elastic-plastic deformation will occur a much lower applied load. The comparison of the measured adhesion forces to the predicted pull-off forces by the JKR theory for elastic behaviour shows a good agreement up to the transition applied load of 1200 nN. This analysis shows that the interaction between the polystyrene surfaces at 65% RH may be adequately described by elastic contact mechanics models up to an applied load of 1200 nN. Above this load, the polystyrene surfaces exhibit elastic-plastic and plastic deformation. The preferential ductility of the material at elevated humidities is associated with the dilution of the surface structure by adsorbed water molecules.

To prove that the deformation caused by the high applied loads and high relative humidity are permanent in nature, a further study was conducted. The polystyrene
surfaces were subjected to applied loads of 4 μN to 31 μN, which were much higher than the previous two studies. Force curves were captured in the order of increasing load and using the same particle on the same position on the polystyrene tablet, force curves were then acquired in the order of decreasing load. The measured adhesion forces increased gradually as the applied load was increased from 4 μN to 31 μN but when the adhesion forces were subsequently measured in descending order of applied load, the adhesion forces were significantly higher compared to the results in ascending order of applied load. This indicates that the contacting surfaces had already deformed plastically as the applied load was increased and a larger contact area is formed between the surfaces. Hence, any further experimentation will yield larger adhesive forces due to this increase in contact area even though the load may be decreasing. In addition to that, further plastic deformation of the surfaces is most likely to occur even for the descending of applied loads because the yield stress is still being exceeded.

There has been evidence in the published literature that cross-linked polystyrene exhibits visco-elasticity (i.e. time-dependency) behaviour. Therefore, a study on the effect of contact time was initiated using the AFM Explorer. The study consisted of three individual set of experiments conducted at three different applied loads of 380 nN, 1500 nN and 5000 nN, at the relative humidity of 65%. At low and medium loads, the increase in contact time did not seem to affect the measured adhesion forces. As the applied load was increased to 5000 nN, a significant increase in adhesion force could be observed as the contact time rose from 0.1 seconds to 10 seconds. This time-dependency of adhesion forces at high loads and high humidities suggests that visco-elastic effects may be a contributing factor to the increase in the adhesion forces at high humidity and high load.

To investigate further the softening behaviour of polystyrene surfaces at high humidities, nanoindentation tests were performed on the material at two separate humidities, 0.1% RH and 65% RH to measure directly the hardness and the Young's modulus of the material. At 0.1% RH, the hardness of the material was found to be essentially constant at a mean value of 0.11 GPa at contact depths of 50 nm and above. At these indentation depths, the hardness value is thought to be most
representative of the true value as surface effects such as surface roughness are diminished. The effective Young's modulus, $E_{gf}$ of the polystyrene sample at 0.1% RH was found to have a mean value of 1.2 GPa at contact depths of 50 nm and above. When the nanoindentation tests were performed at 65% RH, the evaluated hardness of polystyrene falls to a mean value of 0.08 GPa and a mean value of effective Young's modulus is evaluated to be 1 GPa. This result shows that the increase in relative humidity has a significant effect on the mechanical properties of the cross-linked polystyrene. The increase in relative humidity resulted in a 27% decrease in the evaluated hardness of crass-linked polystyrene and a 17% decrease in the effective Young's modulus.

Although the measured values of hardness and effective modulus seemed to differ from published values, the discrepancy in the hardness value reduced significantly when pile-up effects were taken into account. The measured values of hardness are used to predict the applied load at which plastic yield occurs using the model of Maugis-Pollock. Once the effect of pile-up is accounted for, a value of 1030 nN is predicted. This gives excellent agreement with the experimentally observed transition in adhesion.

The behaviour of polystyrene surfaces at varying relative humidity, applied load and contact time has been investigated thoroughly and the results consistently show that these factors significantly influence the adhesion forces of the material. At high applied loads and high relative humidities, the surfaces undergo non-elastic deformation caused by softening of the material as a direct result of adsorbed moisture.
8.3 FUTURE WORK

In view of the experimental results and observations made in this present work, the following recommendations are proposed for future study.

- Investigation into the effects of relative humidity and applied load on a polystyrene particle on particle geometry using the commercial AFM would greatly enhance the understanding of the interactions of polystyrene surfaces.

- A study into the effect of particle size on the force of adhesion between the polystyrene surfaces will strengthen the existing evidence of non-elastic deformation of the contacting regions at high relative humidities and high applied loads.

- There is scope for using the commercial AFM to study the effects of surface roughness of the polystyrene particle and polystyrene tablet on the forces of adhesion at varying relative humidities and applied loads.

- The AFM is also capable of conducting experiments in a liquid environment using a liquid cell. A comparison of adhesion forces between polystyrene surfaces in water and in air will further the understanding of the behaviour of the materials.

- Further development of the nanoindentation technique by AFM is needed to address issues of tip alignment, area function and strain-rate control.

- In light of the experimental evidence that suggests a softening effect on polystyrene surfaces, it would be appropriate to associate the modification of mechanical properties with the sorption characteristics of the material. This could be attempted using a polymer dilution theory such as the Flory-Huggins or Vrentas models.


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Appendix 1

Piezo Calibration Technique

1. Mount a small square piece of silicon on the mounting shoe using super glue or double-sided tape, making sure that silicon is flat on mounting shoe. The silicon acts as a mirror to reflect the laser beam, hence it should be cleaned using mild detergent to remove any grease or contamination.
2. Mount triangular cantilever on a mounting shoe, using super glue, making sure that it is straight and flat on the mounting shoe.
3. Using a spirit level, ensure that laser beam is perpendicular to the back of the cantilever.
4. Focus laser beam on the shorter triangular tip.
5. Place mounting shoe with silicon attached on the piezo platform and using the x, y and z motor driven controller, move the silicon to the furthest edge in order to avoid the cantilever tip from crashing into the silicon when they are moved close together.
6. Manually inspect on the PSD that 2 spots, one reflecting from the back of the cantilever and the other from the silicon, are aligned one on top of the other, the spot of the tip being the one on top.
7. Move the silicon wafer close to the tip by using the x, y, z motor driven controller.
8. Ensure that all overhead fluorescent lights above the instrument are switched off.
9. Move silicon wafer closer to the tip until interference fringes are visible on the HPVEE setup screen.
10. When interference fringes are visible on the HPVEE setup screen, acquire calibration data.
A series of maxima and minima were observed on the HPVEE data acquisition screen representing changes in intensity at the detector due to interference effects between the reflected beams.
Appendix 2
Student's T-test

Student's T-Test was evaluated for the adhesion studies of polystyrene samples. The confidence interval, which denotes the upper and lower limits of the measured values were calculated based on a 90% confidence level. The methodology of the calculation is included in this section and a sample of the tables from which Chapter 6 originate are also presented.

1st Step. Choose a confidence level, \( \gamma \)

2nd Step Determine the corresponding degrees of freedom, \( c \), from Eq. A1.1 and from Table A1

3rd Step Compute the mean \( \bar{x} \) of the sample \( x_1, \ldots, x_n \)

4th Step Compute sample variance, \( s^2 \) by using Equation A1.2

5th Step Compute \( k = C \sigma / \sqrt{n} \)

The confidence interval for \( \bar{x} \) is \( \text{CONF} \{ \bar{x} - k \leq \bar{x} \leq \bar{x} + k \} \)

\[
F(c) = \frac{1}{2} (1 + \gamma) \quad \text{Eq A1.1}
\]

\[
s^2 = \frac{1}{n-1} \left[ (x_1 - \bar{x})^2 + \cdots + (x_n - \bar{x})^2 \right] \quad \text{Eq A1.2}
\]

Sample calculation for adsorption data for Ps_Ad3

1. A confidence level of 90% is chosen.
2. Since \( \gamma = 0.9 \), \( F(c) = 0.95 \). The corresponding degrees of freedom, \( c = 1.9 \) (from Table A1).
3. The mean of the sample of 8 measured values was calculated
4. The sample variance was evaluated using Equation A1.2
5. The upper and lower confidence limits were generated using \( k = C \sigma / \sqrt{n} \), with \( n \) being the number of samples at each relative humidity.
### t-Distribution

Values of $z$ for given values of the distribution function $F(z)$ (see p. 1225)

Example: For 9 degrees of freedom, $z = 1.83$ when $F(z) = 0.95$.

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Appendix 3

Error Analysis

The error analysis for the determination of cantilever spring constant using the Classical Beam Theory (see Section 2.4.1) was conducted using the propagation method. The dimensions of the cantilever were measured using an optical microscope with an error of ± 1 µm and a scanning electron microscope with an error of ± 0.5 µm.

The procedure of the error analysis and the equations used are described in this section.

From Section 2.4.1, the equation for the determination of cantilever spring constant according to the Classical Beam Theory is as follows:

\[ k = \frac{Ew}{4\left(\frac{t}{l}\right)^3} \]  

(2.3)

The symbols \( w, t \) and \( l \) denote the beam width, thickness and length respectively and \( E \) is the Young’s modulus of the material.

The equations used for the error analysis is summarised in Table A3.

| \( q \) = \( x + z \) | \( \frac{\partial q}{\partial x} = \sqrt{\left(\frac{\partial x}{|x|}\right)^2 + \left(\frac{\partial z}{|z|}\right)^2} \) | 1a |
|---|---|---|
| \( q = x - z \) | \( \frac{\partial q}{\partial x} = \sqrt{\left(\frac{\partial x}{|x|}\right)^2 + \left(\frac{\partial z}{|z|}\right)^2} \) | 1b |
| \( q = x \cdot z \) | \( \frac{\partial q}{\partial x} = \sqrt{\left(\frac{\partial x}{|x|}\right)^2 + \left(\frac{\partial z}{|z|}\right)^2} \) | 1c |
| \( q = x / z \) | \( \frac{\partial q}{\partial x} = \sqrt{\left(\frac{\partial x}{|x|}\right)^2 + \left(\frac{\partial z}{|z|}\right)^2} \) | 1d |
| \( q = x^c \) | \( \frac{\partial q}{\partial x} = |C| \frac{\partial x}{|x|} \) | 1e |
| \( q = Cx \) | \( \frac{\partial q}{\partial x} = |C| \frac{\partial x}{|x|} \) | 1f |
Firstly, the error of the product of $E$ and $w$ is evaluated using equation (1c). The uncertainty in $E$ was based on a value of 20% of the typical value (Sader, 1995) and the uncertainty in the measurements of length, width and thickness of the cantilever is based on half of the smallest interval on the scanning electron microscope i.e., 0.5 μm. Next, the error associated with $(Ew/4)$ was calculated using equation (1f).

The uncertainties of $(t/l)$ was calculated using equation (1d) with $\delta t$ and $\delta l$ being 0.5 μm. The uncertainty in the power was evaluated using equation (1c). Finally, the error in the determination of the cantilever spring constant can be calculated by using equation (1c) with $\delta x$ being the error calculated for $(Ew/4)$ and $\delta z$ being the error calculated for $(t/l)^3$.

The results of the error analysis is tabulated below:

Table A4 Error analysis of spring constant determination

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