Free-Radical Polymerization to Create Coated Particles for Interaction Studies:
The Interactions of Amphiphilic Latexes with Surfaces

Stuart W. Prescott,♦ Christopher M. Fellows,♦ Robert F. Considine,* Calum J. Drummond* and Robert G. Gilbert♦*

♦ Key Centre for Polymer Colloids, School of Chemistry, University of Sydney NSW 2006, Australia

* CSIRO Molecular Science, Private Bag 10, Clayton South VIC 3169, Australia

Objectives

- to directly measure the forces between a polymer colloid and various substrates
- to observe the influence of surface modifications on surface interactions

Motivations

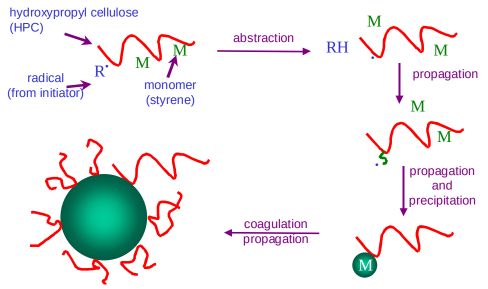
- polymer colloids widely used in paints and adhesives
- adhesive interactions not understood

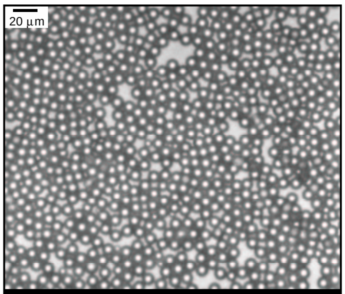
Outline of Poster

1. synthesise large polymer colloid particles
2. attach to an Atomic Force Microscope cantilever
3. measure forces using the AFM
4. explain interactions in terms of intermolecular forces

1 Dispersion Polymerization

- monomer is soluble in solvent, but polymer is insoluble
- latex "precipitates" from solvent (ethanol/methoxyethanol)



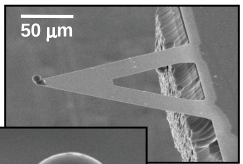


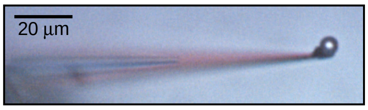
optical micrograph of HPC/PS particles (hydroxypropyl cellulose stabilized polystyrene, average diameter 6.4 µm)

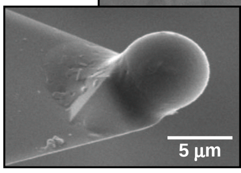
Particles coated with hydroxypropyl cellulose (HPC) chains, ~7 nm² per chain, MW(HPC) = 10^5 (nominal)

2 Preparation of Colloid Probe for AFM

- individual HPC/PS particles were picked up using a micro-manipulator under an optical microscope
- particles were glued to AFM cantilever using Epikote™ 1004 resin (on a hot-stage) or Araldite™ at room temperature





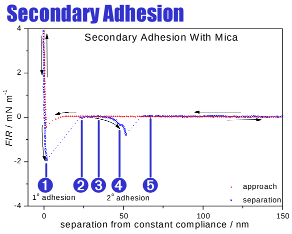


Optical and scanning electron micrographs of the particles mounted on the AFM cantilevers.

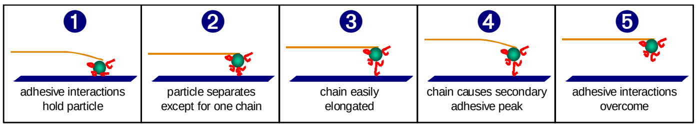
3 Force Measurement

- interactions of HPC/PS particles with mica, silica & graphite measured
- colloid probe pushed against substrate (in KNO_3 solution) then pulled off
- scan rate 1 Hz, scan size 600 nm, approach to surface 400nm

Secondary Adhesion

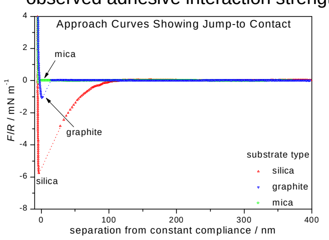


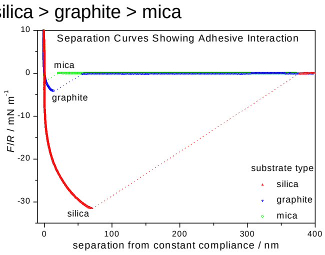
- typical force curve shown on left
- one chain remains attached to substrate and pulls off later (schematic below)
- secondary adhesion provides direct evidence of HPC–substrate interactions
- this phenomenon has also observed in other systems (polymer solutions)[1]



Approach and Separation

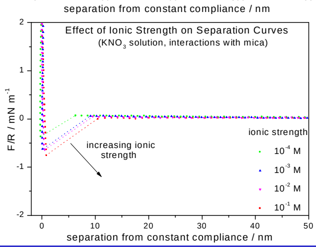
- attractive particle–substrate forces cause jump-to contact (starts between 12 nm and 100 nm)
- adhesion of particle to substrate gives an adhesive hysteresis – approach and separation curves different
- observed adhesive interaction strength: silica > graphite > mica





Effect of Ionic Strength

- surface interactions observed as ionic strength varied (10^{-4} to 10^{-1} M KNO_3)
- measured jump-to contact started at longer distances at higher ionic strength
- in most other systems, interaction distances shorter at higher ionic strength



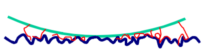
4 Surface Interactions Explained

Jump-to Contact

- HPC "hairs" on particle associate with substrate surface; random motions "reel" particle in, bring surfaces together quickly
- in *dilute* solution, HPC chains calculated to penetrate up to 50 nm into water; chains on particles are *not dilute* so will extend further

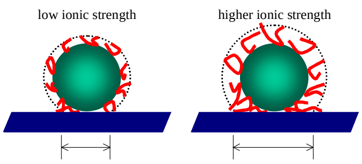
Surface Roughness

- hairy layer is easily deformable so chains can extend into surface roughness



- normally, surface roughness decreases contact area hence decreases adhesive strength;[2] here it *increases* contact area and adhesive strength (due to deformable surface layer)

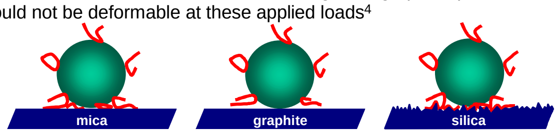
Ionic Strength



- HPC chains are more extended in salt solutions (up to 1 M ionic strength)[3]
- elongated HPC chains touch surface over larger surface area, giving stronger adhesion to surface

Summary of Observations

- observed interactions are unlike those of pure polystyrene or pure HPC
- direct evidence for hairy-layer–substrate interactions was observed:
  - secondary adhesion of HPC chain and surface
  - increased ionic strength gives greater adhesion
- adhesive strength was increased by a rough substrate surface and an easily deformable surface modification on the particle
- particle core is also involved in adhesion *e.g.* with graphite; particle core should not be deformable at these applied loads[4]



Conclusions

- HPC/PS particles are "compatibilized"
  - they adhere to both hydrophobic and hydrophilic surfaces
  - their properties are a combination of the uncoated polymer (polystyrene) and the coating (hydroxypropyl cellulose); both particle core and hairy layer are significant in interactions
- interaction strength can be varied by roughening surface or elongating surface hairs

References

1. Senden, T. J.; Dimeglio, J. M.; Auroy, P. *European Phys. J. B* **1998**, *3*, 211-216.
2. Schaefer, D. M.; Carpenter, M.; Gady, B.; Reifenberger, R.; Demejo, L. P.; Rimai, D. S. *J. Adhesion Sci. Technol.* **1995**, *9*, 1049-1062.
3. Suto, S.; Nishibori, W.; Kudo, K.; Karasawa, M. *J. Appl. Polym. Sci.* **1989**, *37*, 737-749.
4. Biggs, S.; Spinks, G. *J. Adhesion Sci. Technol.* **1998**, *12*, 461-478.

Acknowledgements

- A/Prof. G.G. Warr, Dr Jamie Schulz and Mr Gordon Burns (University of Sydney) for access to the AFM and light microscopes as well as many enlightening discussions
- Mr Tony Romeo (Key Centre for Microscopy and Microanalysis) for assistance with SEM work
- The Key Centre for Polymer Colloids is established and supported under the Australian Research Council's Research Centres Programme