

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



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Objectives

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

Motivations

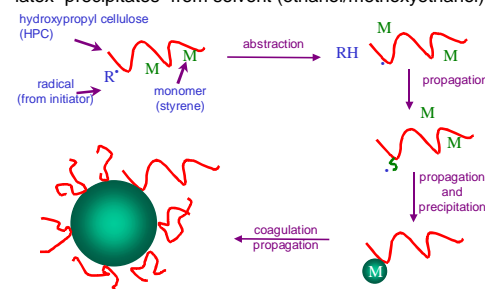
- polymer colloids widely used in paints and adhesives
- adhesive interactions not understood

Outline of Poster

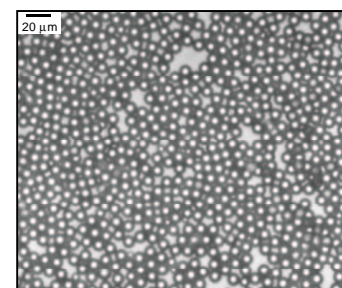
- synthesise large polymer colloid particles
- attach to an Atomic Force Microscope cantilever
- measure forces using the AFM
- explain interactions in terms of intermolecular forces

1 Dispersion Polymerization

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



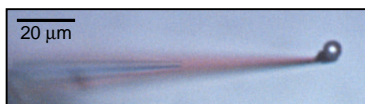
Particles coated with hydroxypropyl cellulose (HPC) chains, $\sim 7 \text{ nm}^2$ per chain, MW(HPC) = 10^5 (nominal)



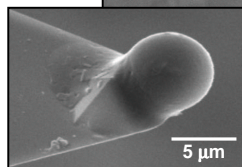
optical micrograph of HPC/PS particles (hydroxypropyl cellulose stabilized polystyrene, average diameter 6.4 μm)

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.



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

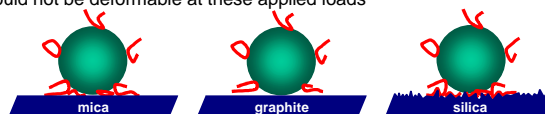
- hairy layer is easily deformable so chains can extend into surface roughness
- normally, surface roughness decreases contact area hence decreases adhesive strength;² here it *increases* contact area and adhesive strength (due to deformable surface layer)

Ionic Strength

- low ionic strength
- higher 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 loads⁴



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

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

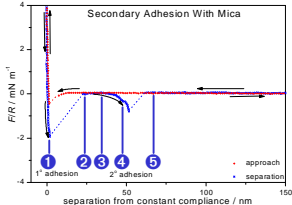
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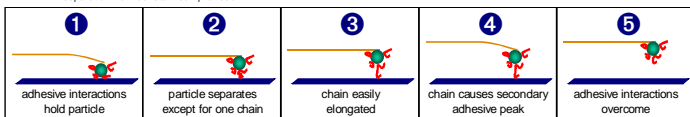
3 Force Measurement

- 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

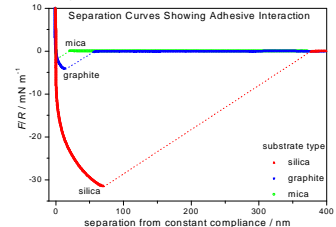
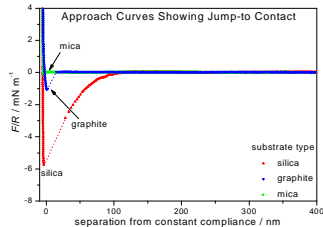


- typical force curve shown on left
- one chain remains attached to substrate and pulls off later (schematic below)
- secondary adhesion provides direct evidence of HPC–substrate interactions
- this phenomenon has also observed in other systems (polymer solutions)¹



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

