Synthesis and Film Formation of Emulsion Polymer Latexes Featuring H-Bonding via Janus Guanine-Cytosine Base Monomer

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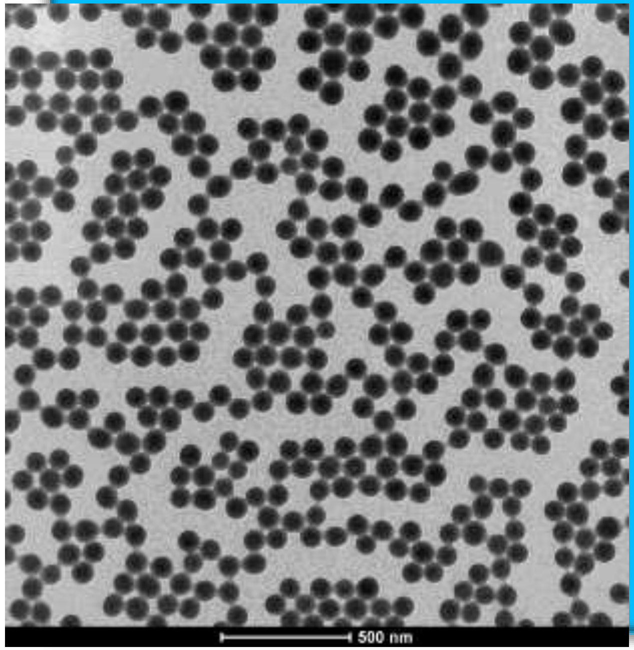
Film formation and mechanical properties of emulsion polymers

Advantages

- Water Based
- High solids content (>50%)
- Fast and full conversion of monomers
- Control particle size and morphology
- Easy to tailor polymer properties

Emulsion Polymers

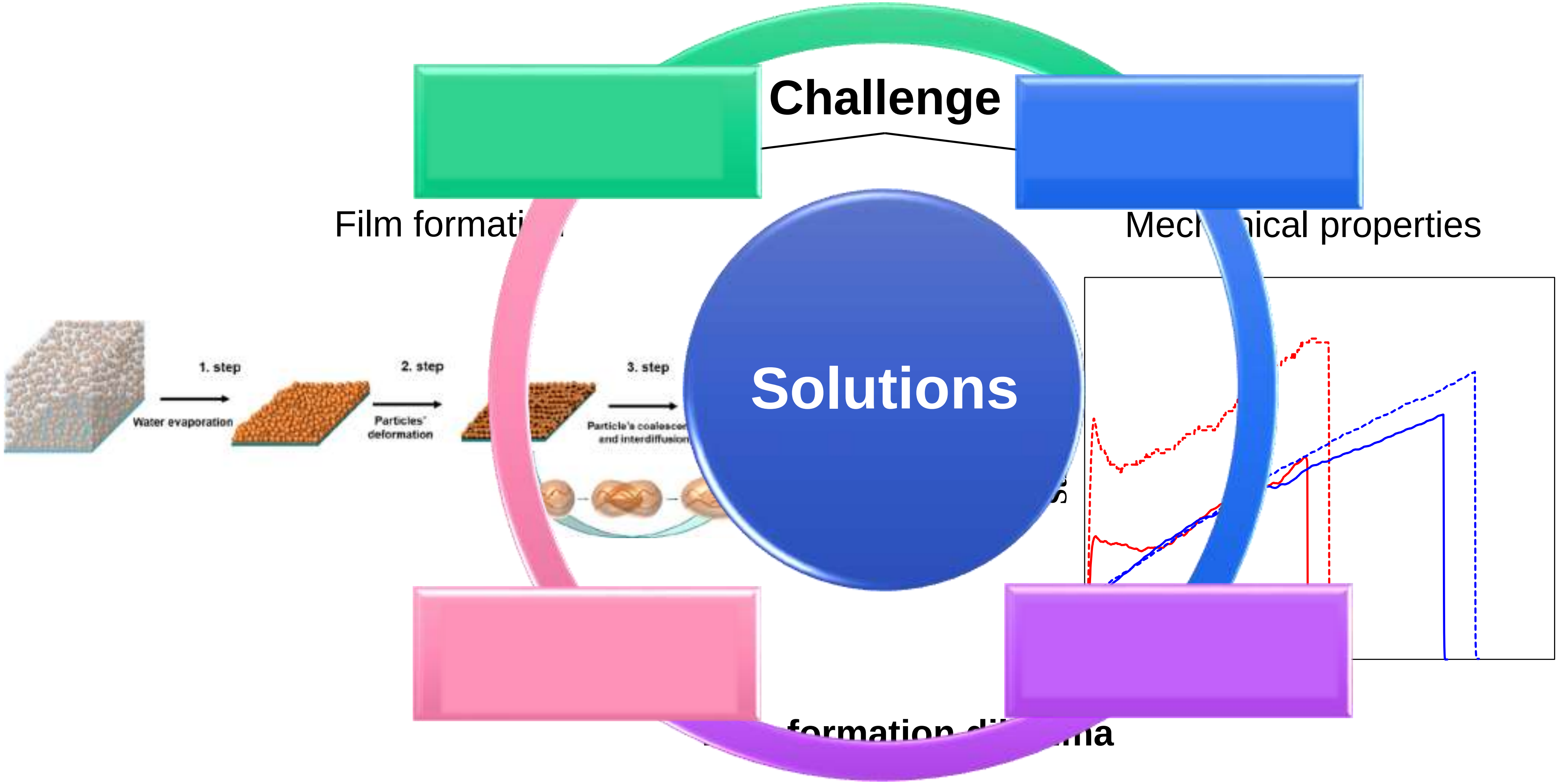
Uses



nm to µm sized particles dispersed in water

Aguirre, M. *et. al.* Polymer Colloids: Current Challenges, Emerging Applications, and New Developments. *Macromolecules* **2023,** *56* (7), 2579-2607.

Film formation and mechanical properties of emulsion polymers



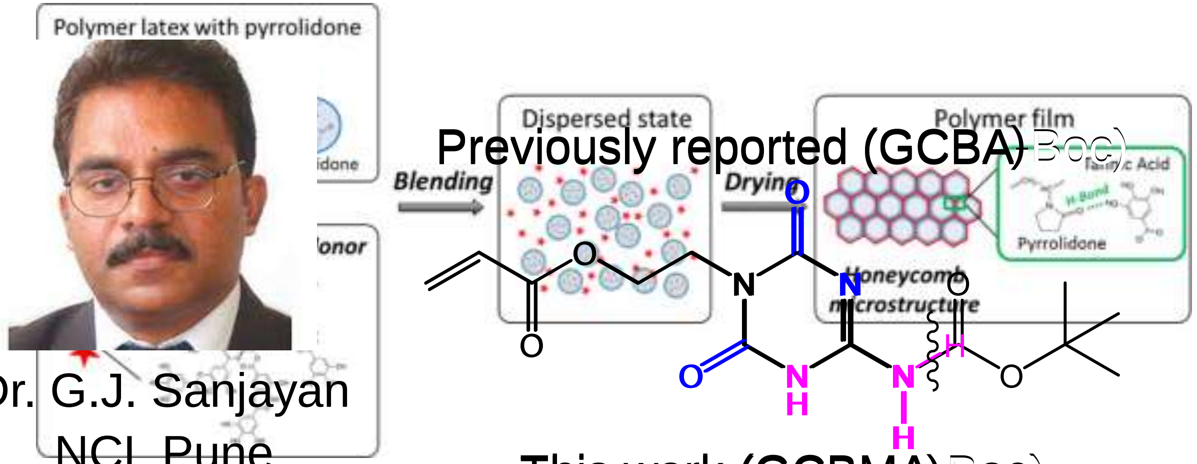
Aguirre, M. *et. al.* Polymer Colloids: Current Challenges, Emerging Applications, and New Developments. *Macromolecules* **2023,** *56* (7), 2579-2607.

H-bonding and guanine-cytosine base (GCB) monomers

H-bonding to reinforce films without sacrificing film formations

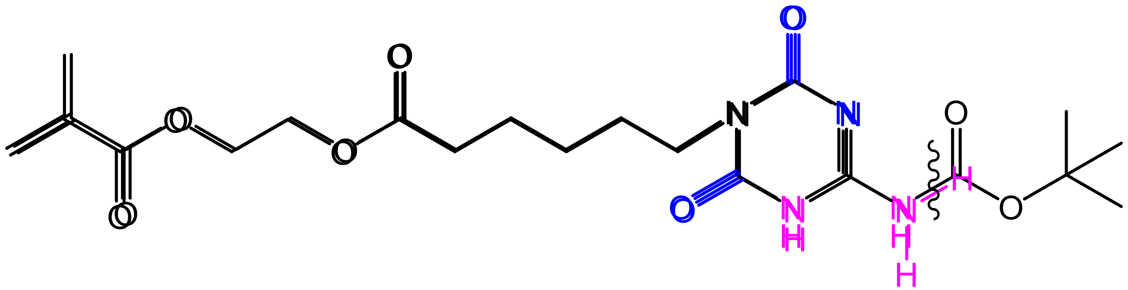
Guanine-cytosine base (GCB) monomers

Dimer base pairs



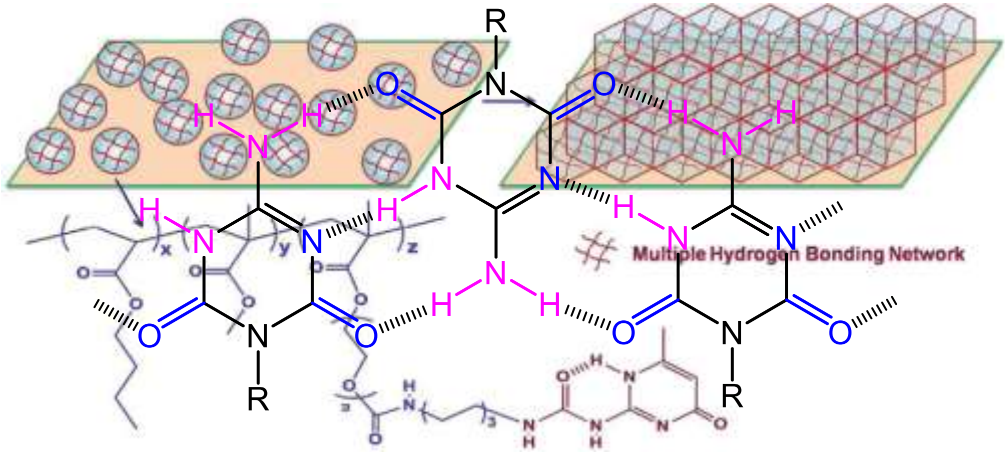
Dr. G.J. Sanjayan
NCL Pune

This work (GCBMA-Boc)



Self-complementary units

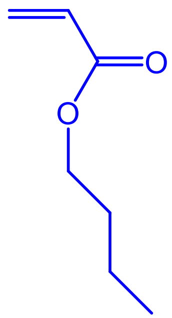
AAD-DDA triple H-bonding array



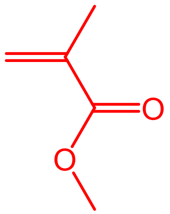
Jiménez, C. L. et al., … Acids, and Smart Polymers. *J. Org. Chem.* **2021**, 86 (21), …
Chen, Y. et al., Multiple Hydrogen Bond Array Reinforced Cellular Polymer Films from Colloidal Crystalline Assemblies of Soft Latex Particles. *ACS Macro Letters* **2012** *1* (5), 603-608

Surfactant free emulsion polymerization of BA/MMA/GCBMA-Boc

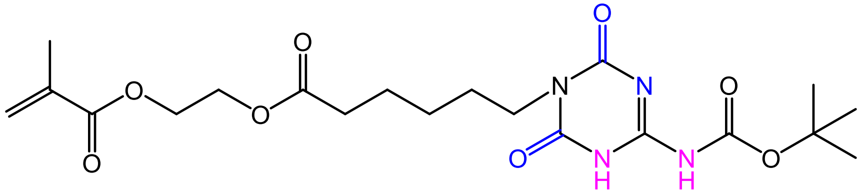
BA



MMA



GCBMA-Boc

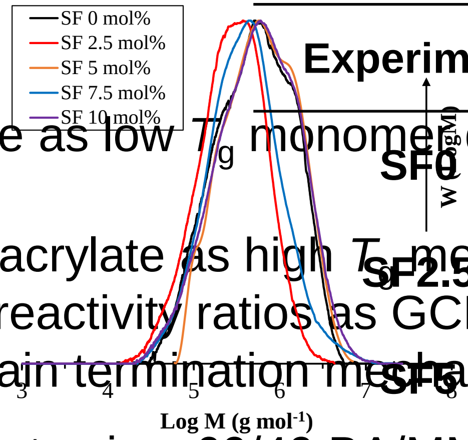


70^{o}C, KPS

10% SC in water

- Butyl acrylate as low T_g monomer due to good adhesive properties
- Methyl methacrylate as high T_g monomer
  - Similar reactivity ratios as GCBMA-Boc
  - MMA main termination mechanism is disproportionation
- Initial base latex is a 60/40 BA/MMA ratio
- Surfactant free to avoid negative aspects of surfactant in film formation

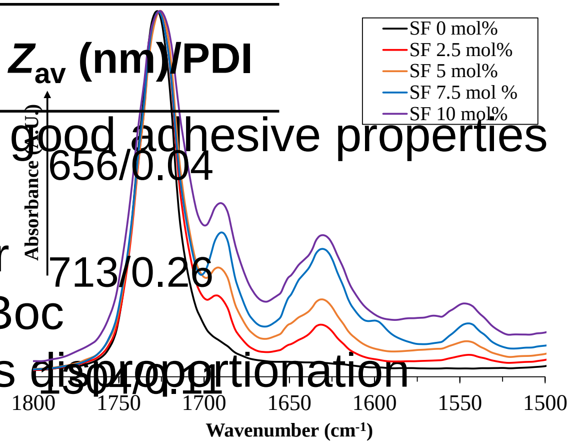
MWDs



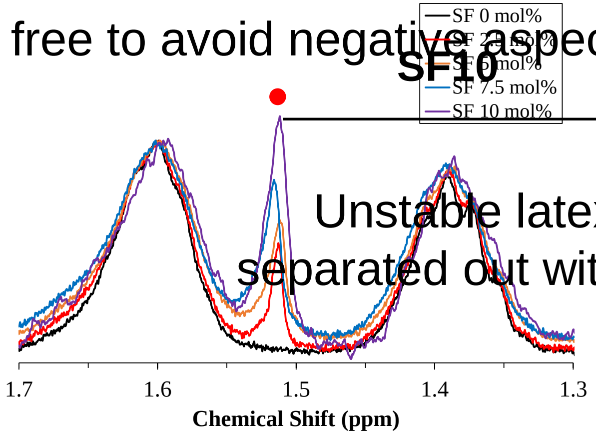
DLS Results

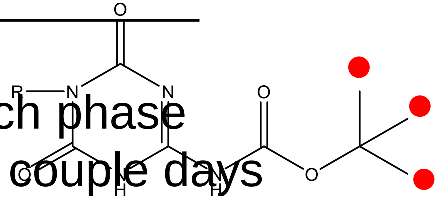
Experiment	Z_{av} (nm)/PDI
SF0	656/0.04
SF2.5	713/0.26
SF5	1504/0.11
SF7.5	814/0.24
SF10	832/0.20

IR Spectra



NMR Spectra

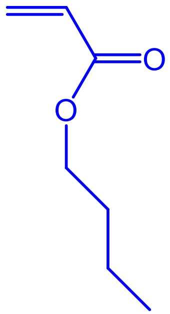




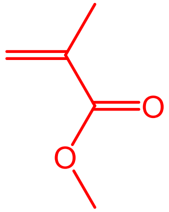
Unstable latex which phase separated out within a couple days

Conventional emulsion polymerization of BA/MMA/GCBMA-Boc

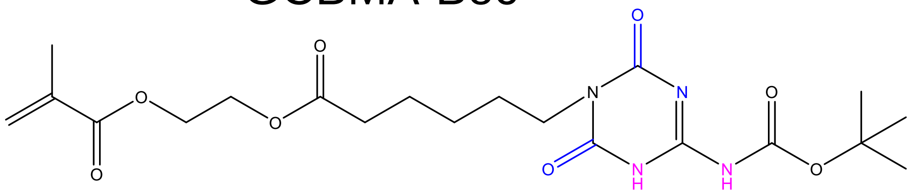
BA



MMA



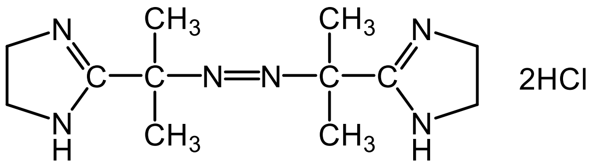
GCBMA-Boc



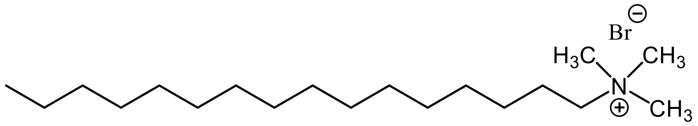
Low reaction temperature

- Minimise BA backbiting
- Reduce chance of deprotection of GCBMA-Boc

Initiator: VA-044



Surfactant: CTAB

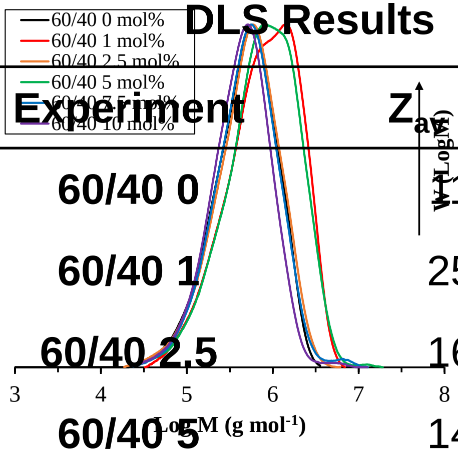


Temperature: 50°C

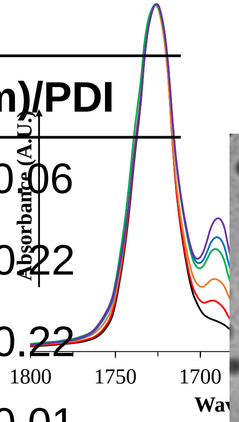
Conventional emulsion polymerization of BA/MMA/GCBMA-Boc

60/40 BA/MMA

MWDs



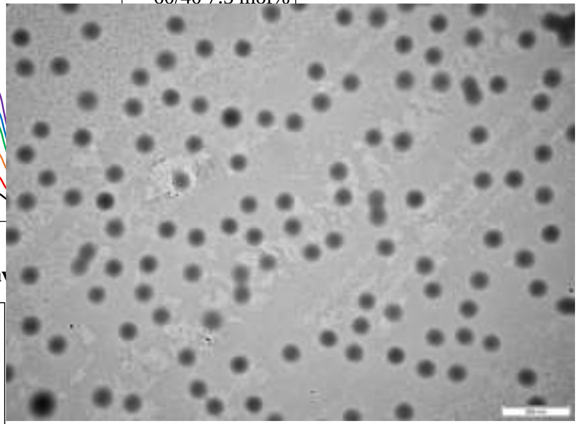
IR Spectra



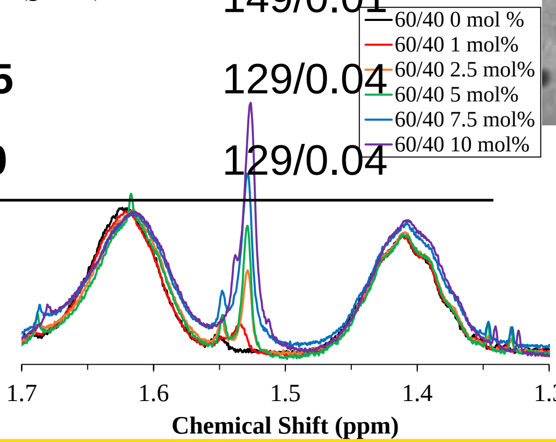
DLS Results

Experiment	Z_{av} (nm)/PDI
60/40 0	119/0.06
60/40 1	251/0.22
60/40 2.5	167/0.22
60/40 5	149/0.01
60/40 7.5	129/0.04
60/40 10	129/0.04

TEM of 60/40 5

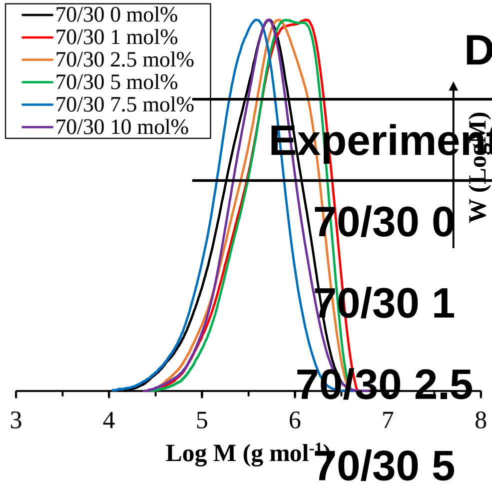


NMR Spectra

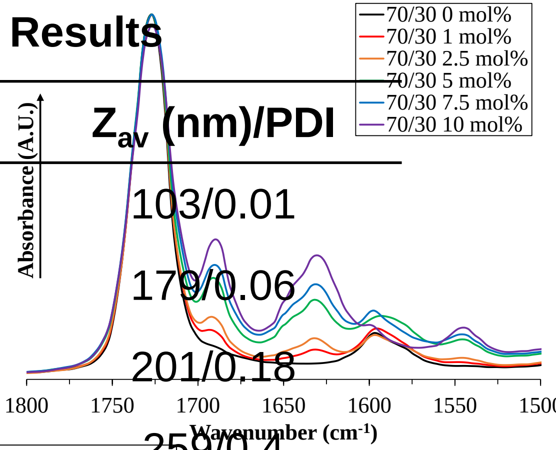


70/30 BA/MMA

MWDs



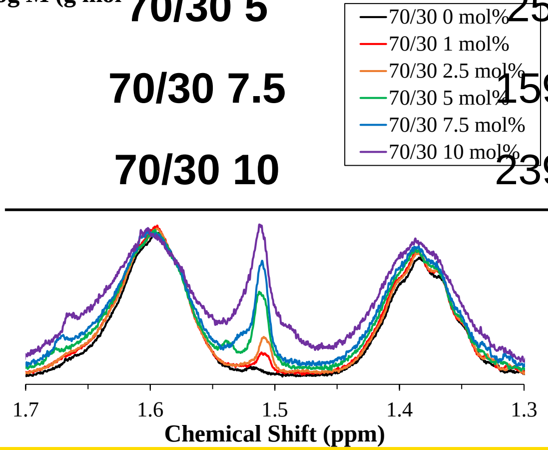
IR Spectra



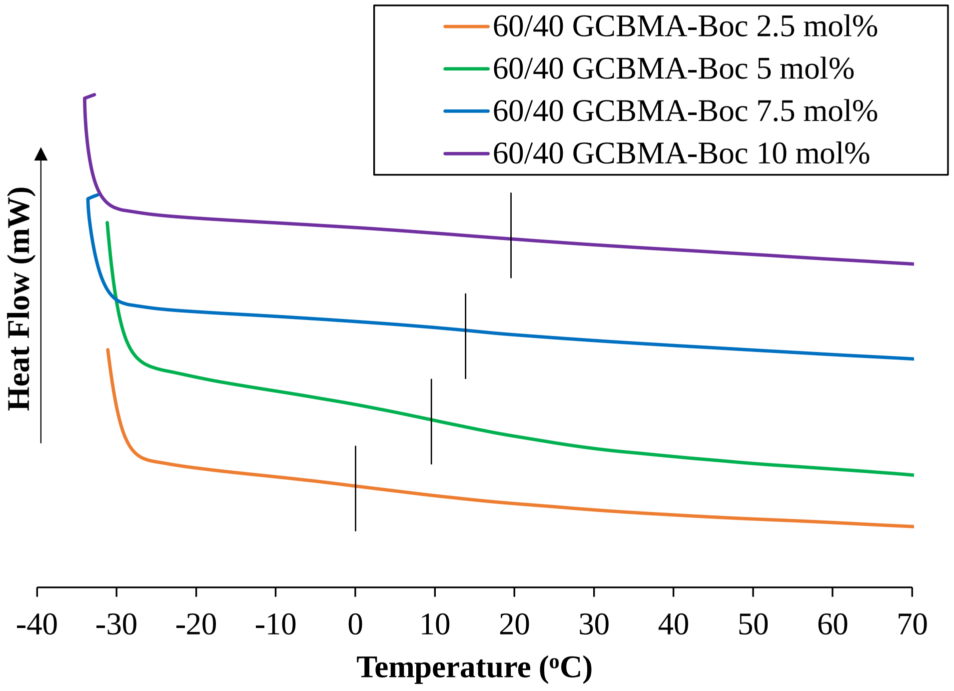
DLS Results

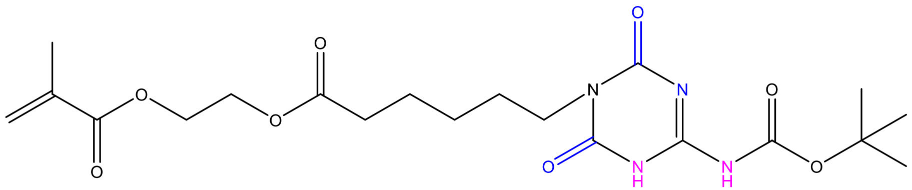
Experiment	Z_{av} (nm)/PDI
70/30 0	103/0.01
70/30 1	179/0.06
70/30 2.5	201/0.18
70/30 5	259/0.4
70/30 7.5	159/0.02
70/30 10	239/0.05

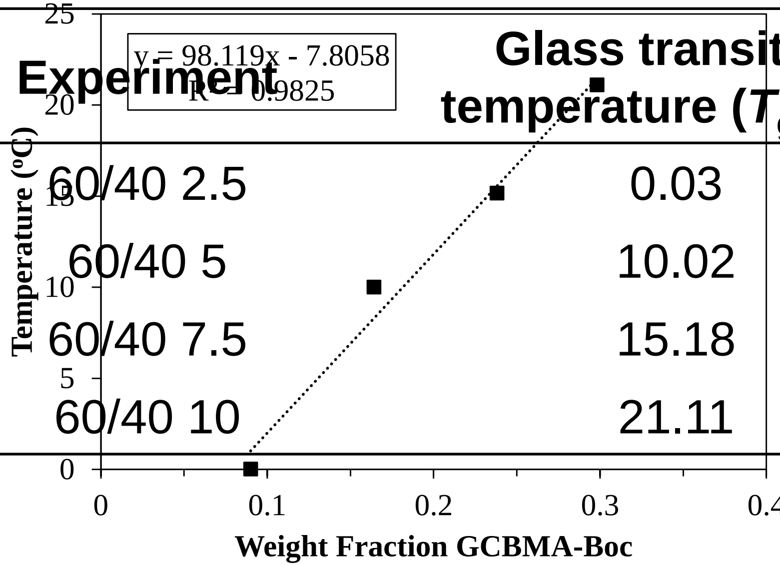
NMR Spectra



Glass transition temperature increases with GCBMA-Boc content



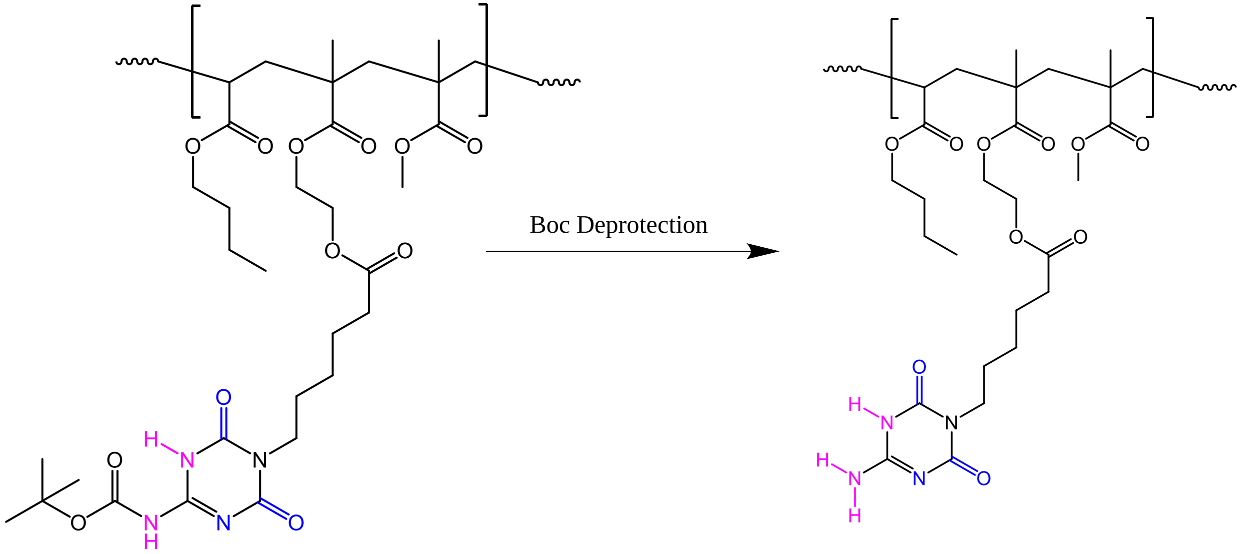




Experiment	Glass transition temperature (T_g) (°C)
60/40 2.5	0.03
60/40 5	10.02
60/40 7.5	15.18
60/40 10	21.11

T_g of P(GCBMA-Boc) = 90°C

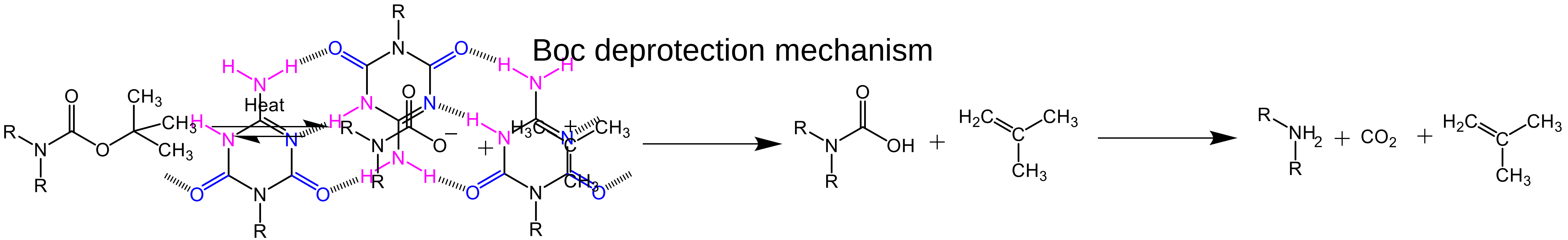
Film formation and Boc deprotection



Self-complementary triple H-bonding

- Typically, Boc deprotection procedures done using TFA/DCM (50/50 v/v) or conc. HCl
- Requires dissolution and destruction of the beneficial particle structure
- BOC protected latexes film formed directly from latex and then deprotected via heat

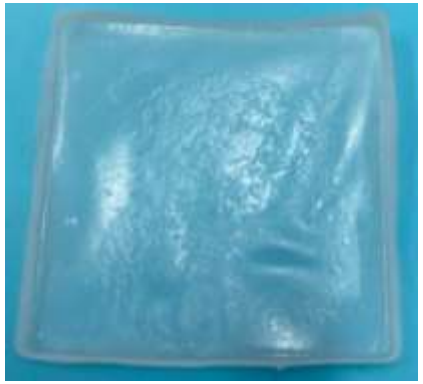
Boc deprotection mechanism



Film formation and Boc deprotection

Film formation done at 40^{o}C in a silicone mold

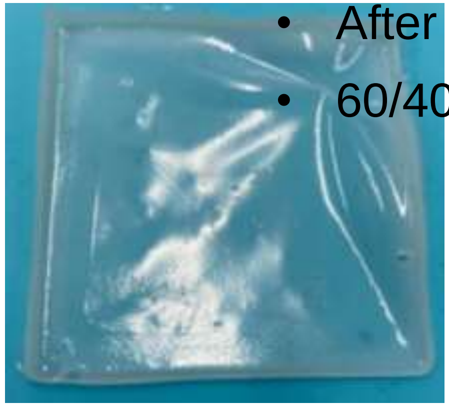
60/40 0



60/40 5

60/40 10

70/30 0



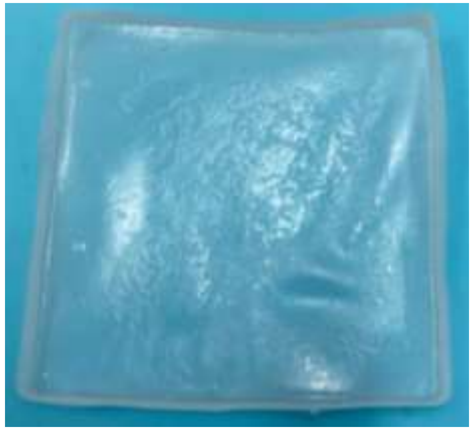
70/30 5

70/30 10

- Films formed up to 10 mol% for 60/40 series
- After addition of GCBMA the transparency was lost
- 60/40 7.5 and 60/40 10 were very brittle and broke easy under handling

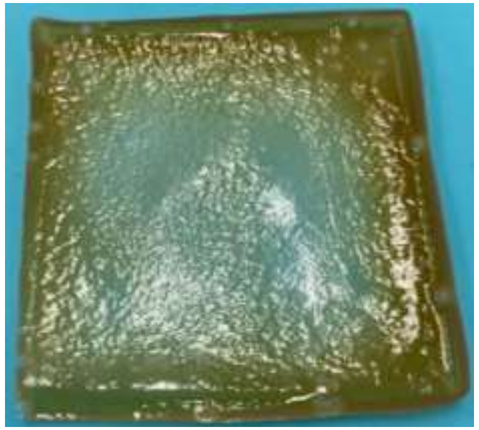
Film formation and Boc deprotection

60/40 0

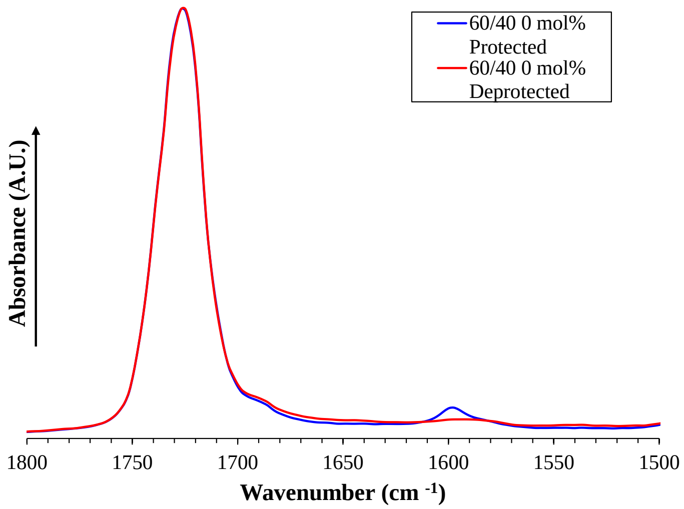


Annealing/
Deprotection

130°C, 48 h



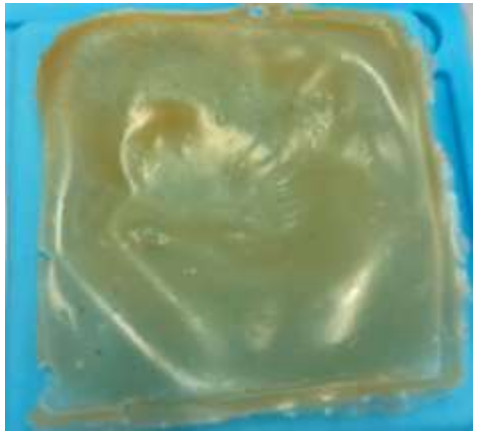
IR Spectra

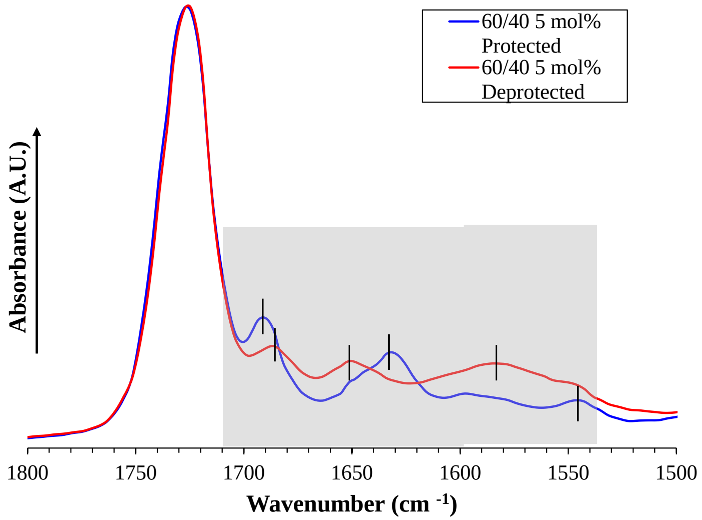


60/40 5

Annealing/
Deprotection

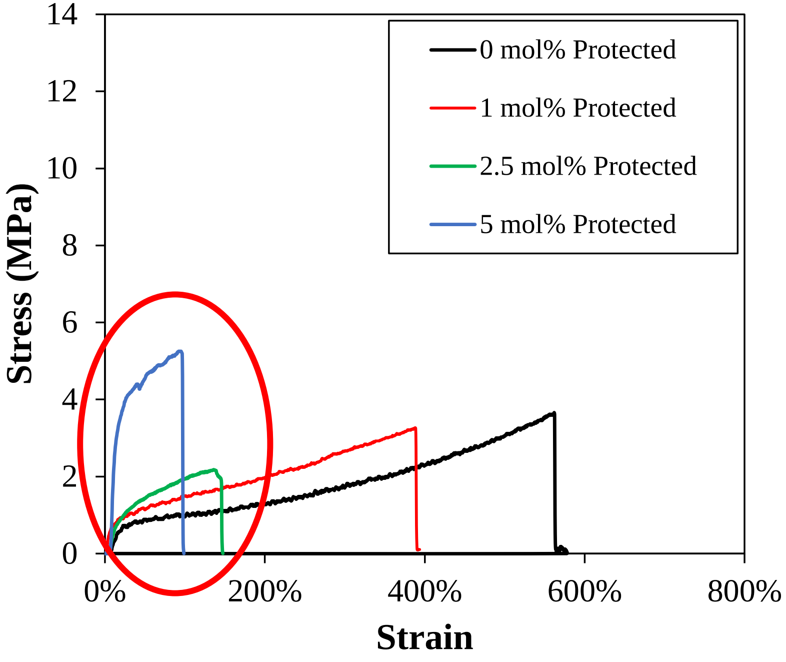
130°C, 48 h



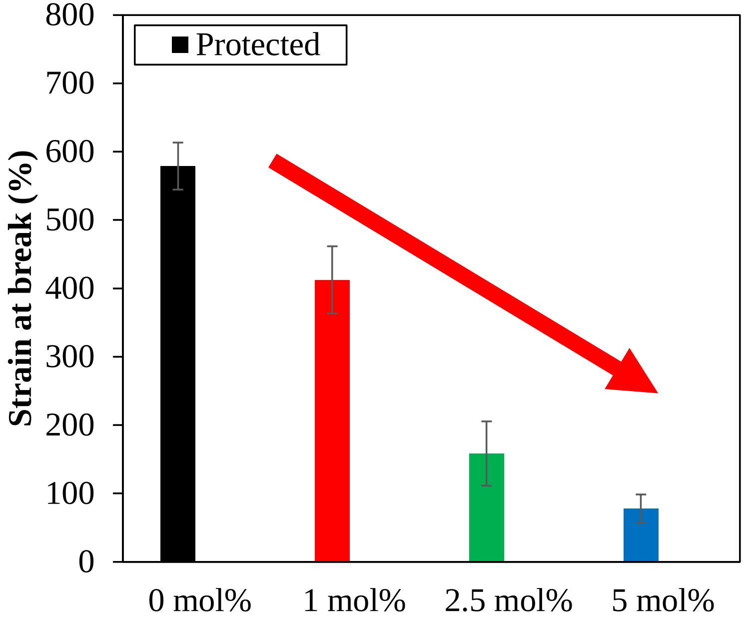


Mechanical Properties of 60/40 BA/MMA Series

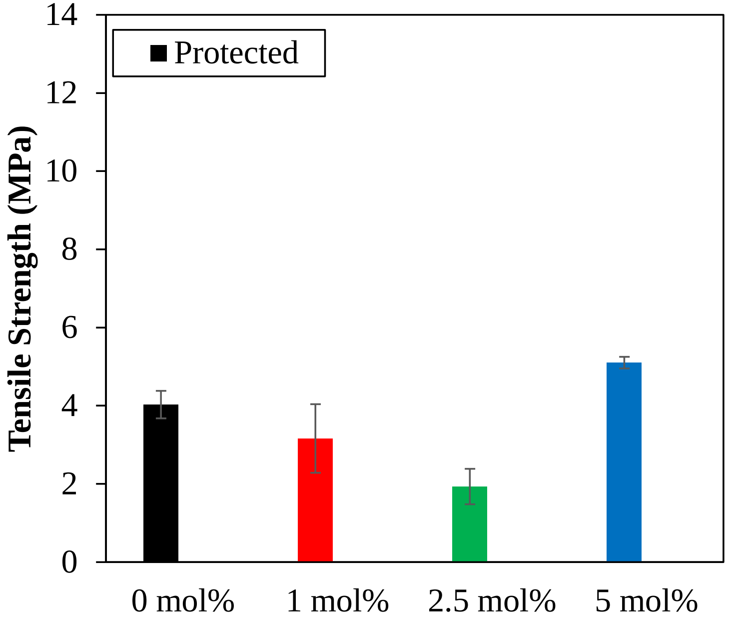
Representative stress-strain curves



Strain at break



Tensile strength



Steeper initial elastic deformation with increasing GCBMA-Boc content

Reduced strain at break with increasing GCBMA-Boc content

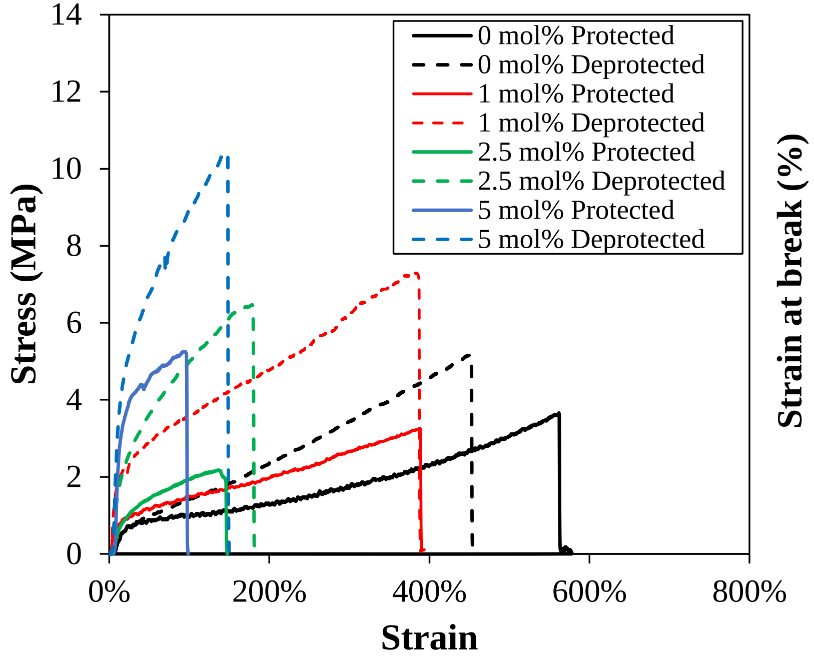
Overall, incorporation of GCBMA-Boc leads to a more brittle film

Only 5 mol% GCBMA-Boc has increased tensile strength

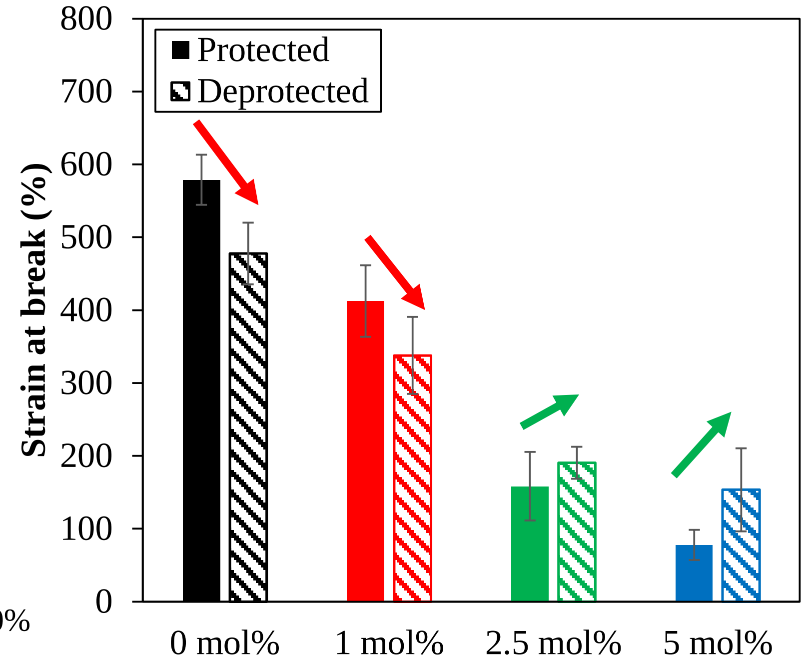
UNSW SYDNEY

Mechanical Properties of 60/40 BA/MMA Series

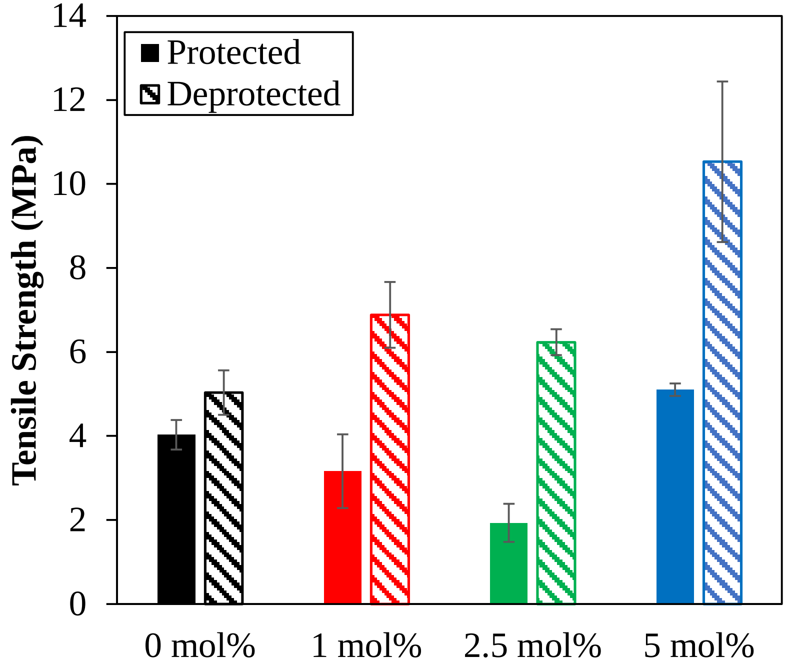
Representative
Stress-strain curves



Strain at break



Tensile strength

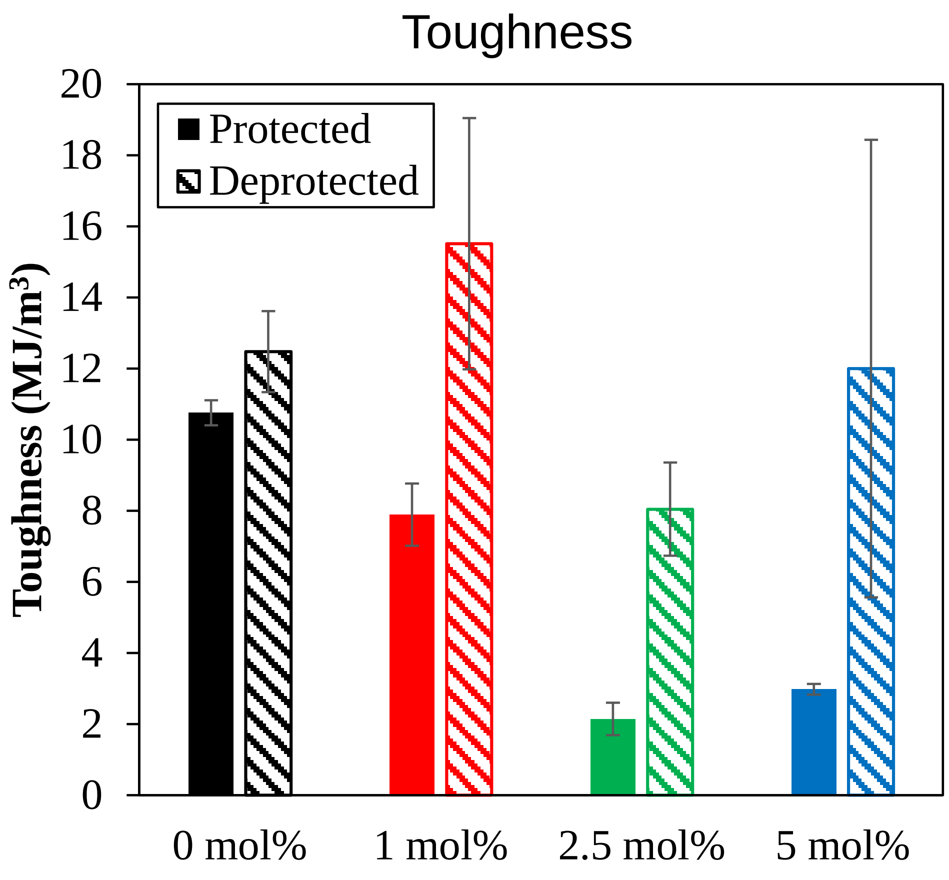


Clear effect of annealing/deprotecting on mechanical properties

Strain at break increases for higher mol% GCBMA

Deprotection leads to large increase in tensile strength

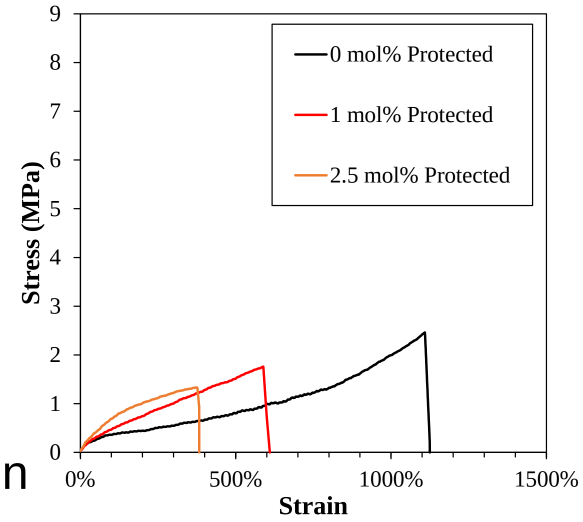
Mechanical Properties of 60/40 BA/MMA Series

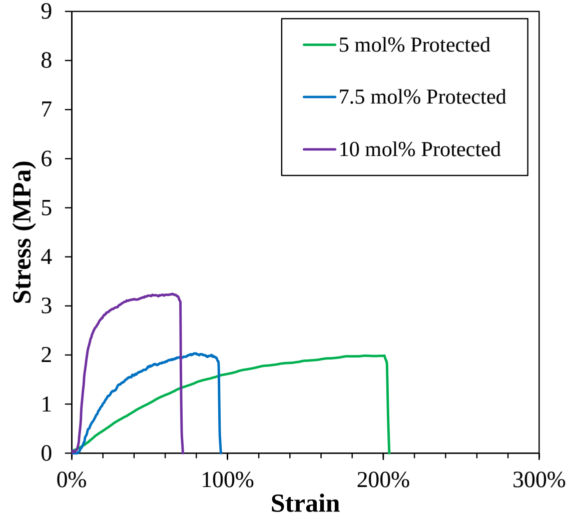


Overall, 1 mol% GCBMA incorporation resulted in the best film

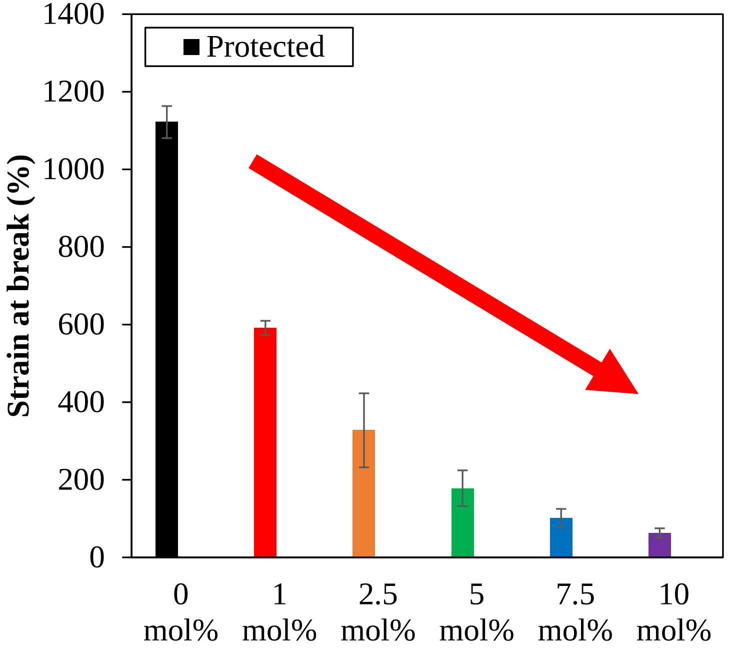
Mechanical Properties of 70/30 BA/MMA Series

Stress-strain curves



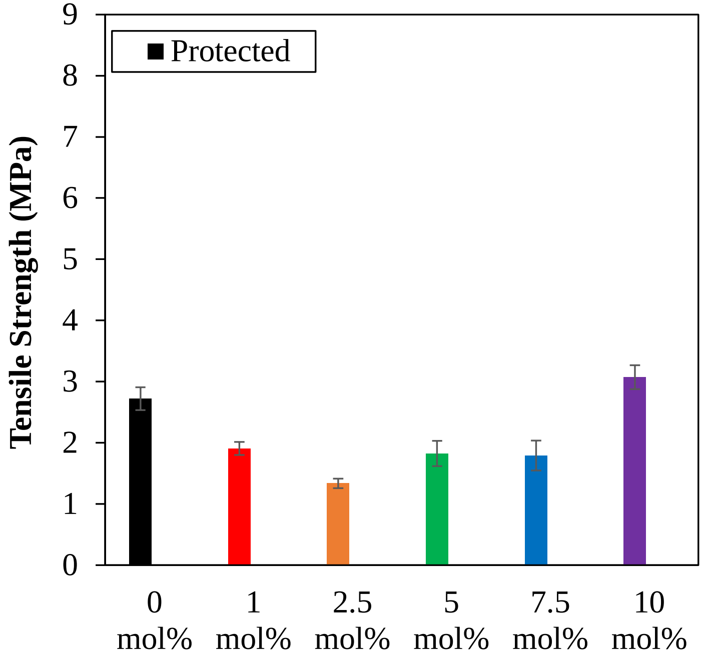


Strain at break



Once again reduced strain at break with increasing GCBMA-Boc content

Tensile strength

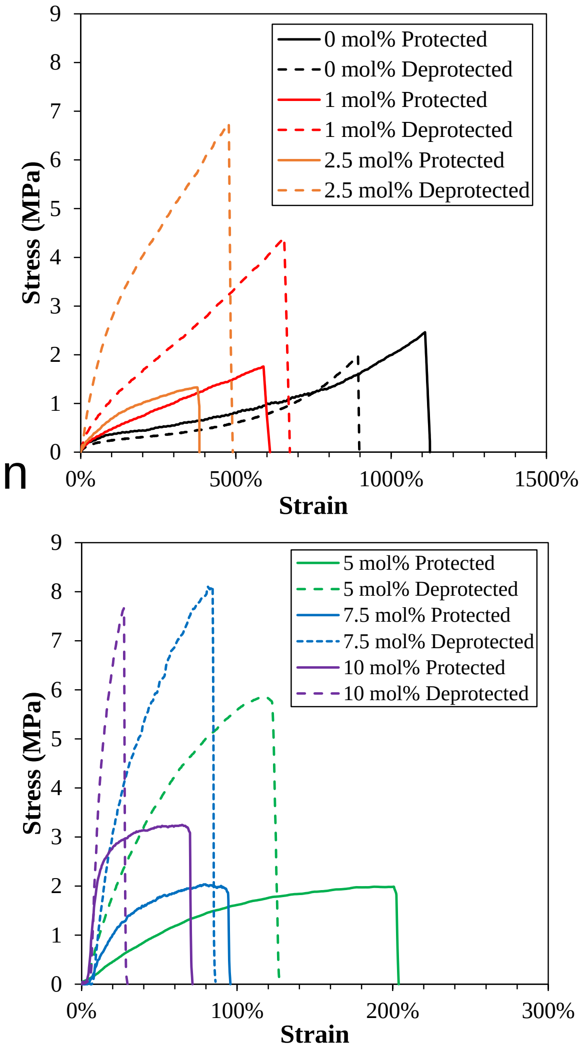


Only 10 mol% GCBMA-Boc has increased tensile strength

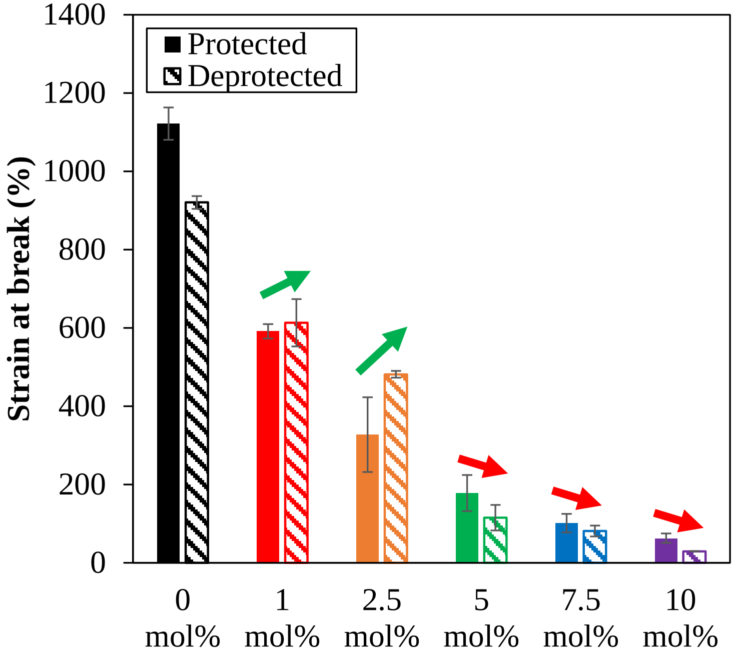
UNSW SYDNEY

Mechanical Properties of 70/30 BA/MMA Series

Stress-strain curves

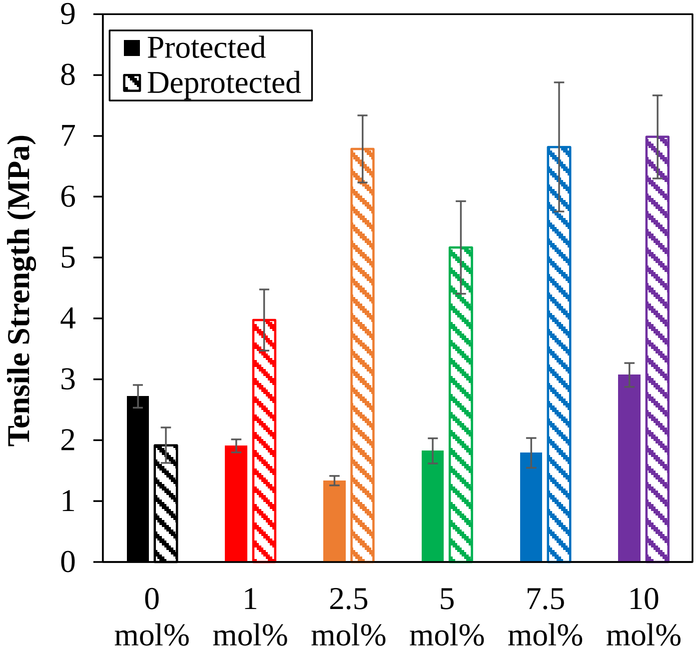


Strain at break



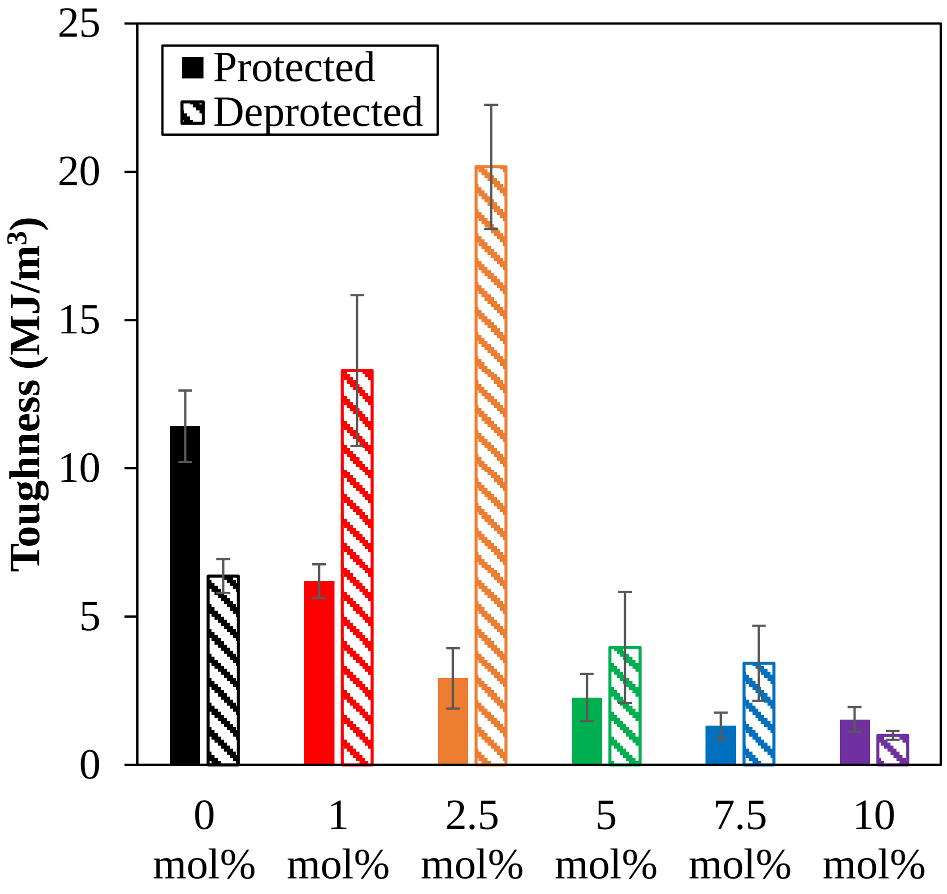
1 mol% and 2.5 mol% GCBMA have increased strain at break compared to GCBMA-Boc films

Tensile strength



Large increase in tensile strength at 2.5 mol% GCBMA but no further gains with higher incorporation

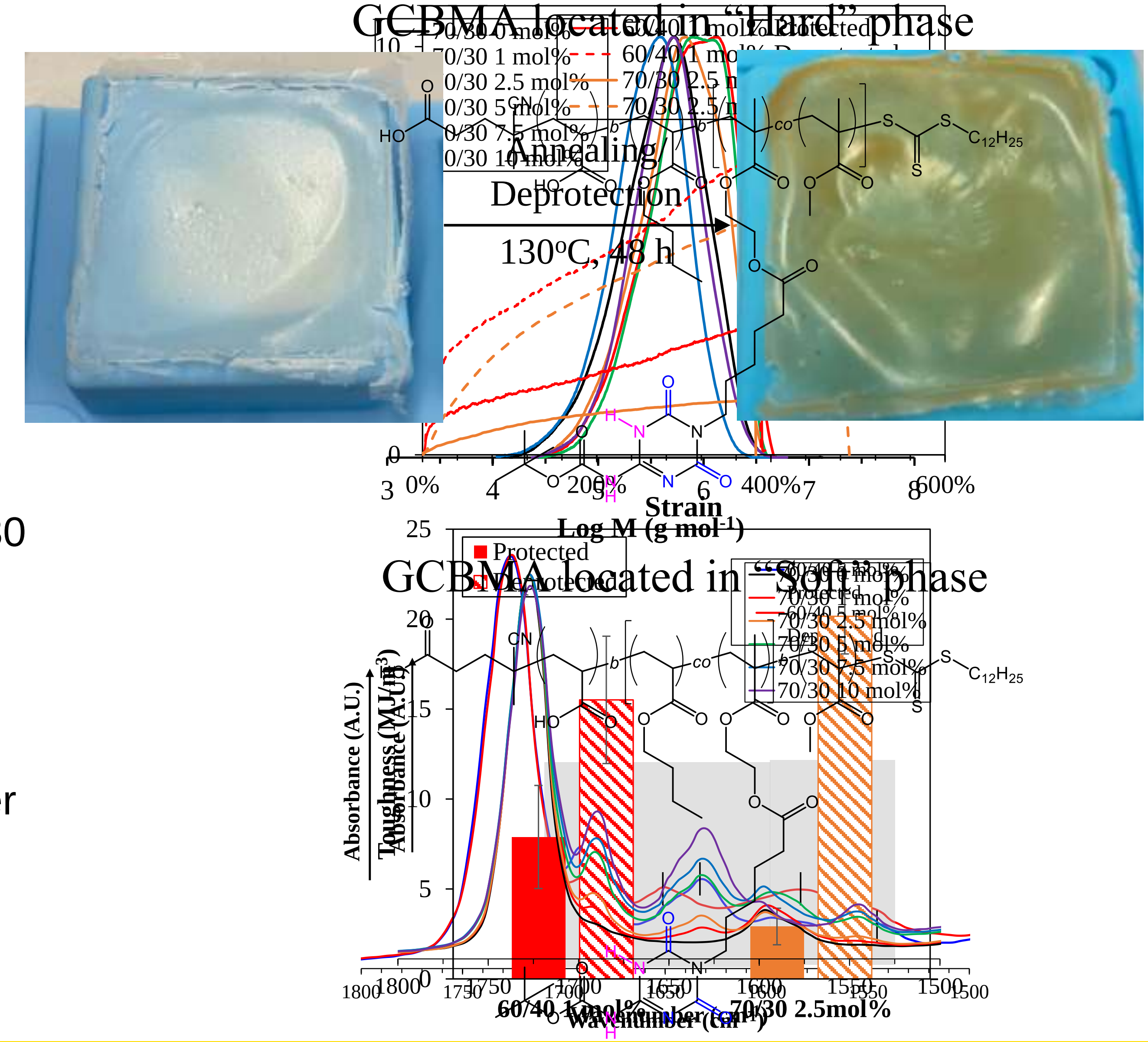
Mechanical Properties of 70/30 BA/MMA Series



- With 2.5 mol% incorporation of GCBMA resulted in the toughest film with large increase compared with base latex
- At 2.5 mol% and below, beneficial effects of hydrogen bonding result in stronger and tougher films
- Above 2.5 mol%, the detrimental effects of the high T_g nature of the GCBMA monomer result in weaker films
- An initial high elasticity latex formulation gains the most from GCBMA incorporation

Conclusions

- Successful copolymerization of GCBMA with BA/MMA in emulsion
- Film formation of latexes and successful deprotection of Boc protecting group
- With 1 mol% for 60/40 and 2.5 mol% for 70/30 GCBMA resulted in remarkable increase in mechanical properties
- Future works involving controlled polymerization to isolate GCBMA within either “Hard” or “Soft” Block



Acknowledgments

Academy of Scientific & Innovative Research
Set up by an Act of Parliament, An Institute of National Importance

Joanna Li
Prof Per B. Zetterlund

Dharmendra Singh
Prof. Gangadhar J. Sanjayan

THANK YOU