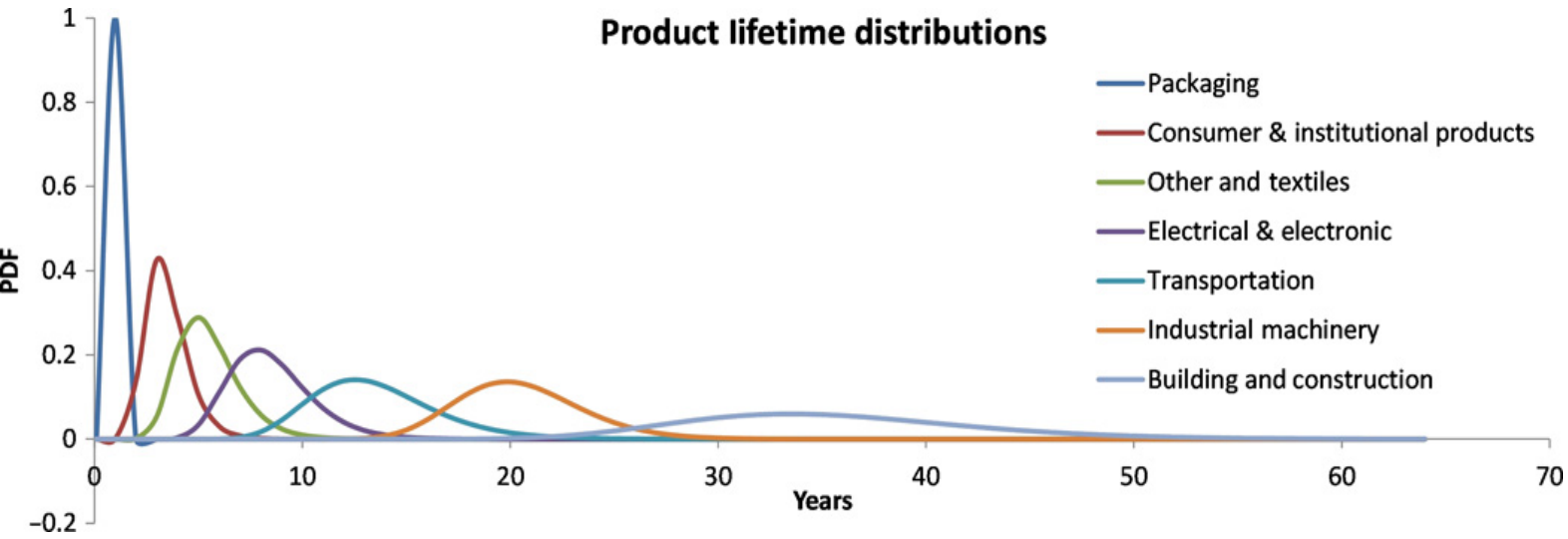
Hydrophobic Modification of Starch for Green Plastics Application

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UNIVERSITY OF WATERLOO
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Introduction



Geyer et al. Sci. adv, 2017

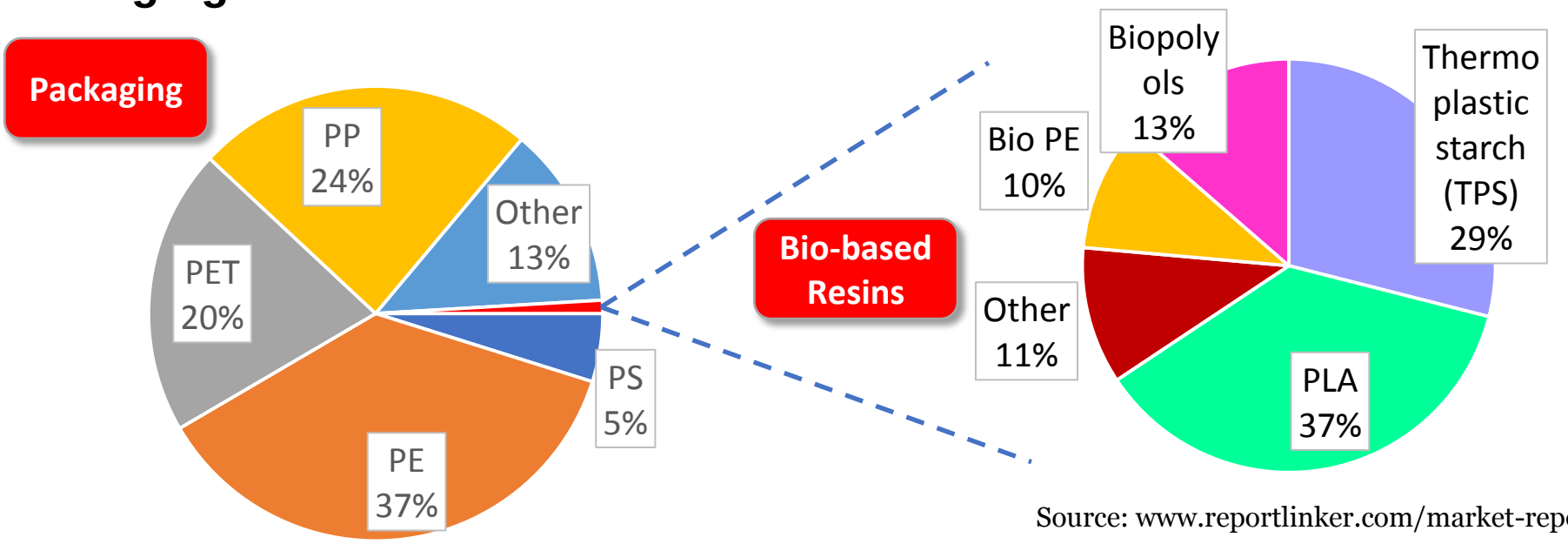
- Commodity plastics are made from PP, PE, PET, PS, etc., which are non-biodegradable
- These plastics have a short service period and end up as waste after single use
- Alternative: Starch: renewable, abundant, biodegradable, inexpensive and easily modified
- Challenge: Hydrophilic, brittle, poor melt processability



Source: Greenpeace.org.uk

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Packaging market



Source: www.reportlinker.com/market-report/

Incumbent Resins

Attributes

- Optical Clarity
- Mechanical Properties
- Elongation/Stretch
- Barrier

Process/Costs

- Direct Conversion (Melt process)
- Resin Cost: ~ $2/kg

Bio-based Resins:

Attributes

- Close to Incumbent Properties
- Barrier Gaps
- **Renewable**
- **Biodegradable / Compostable**

Process/Costs

- Adjusted Direct Conversion
- Resin Cost: ~ $3-6/kg

Thermoplastic polysaccharides opportunities

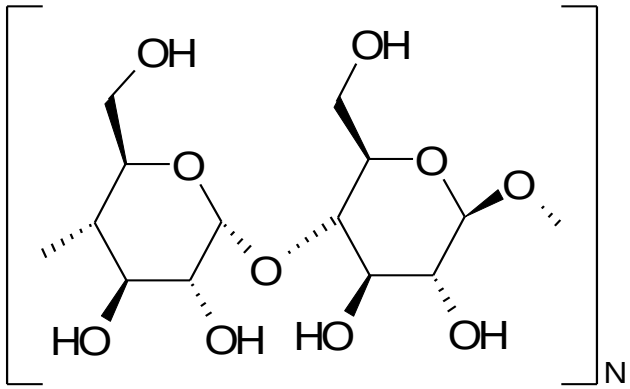
Cellulose thermoplastics

- Materials have good physical properties, are clear, dye-able, and have a nice aesthetic feel
  - The cost of cellulose thermoplastics limit their market share
  - Low solubility of cellulose limits the derivatization chemistry

Starch thermoplastics

- Starch can be made melt-processable using water / glycerol plasticizers
  - Materials properties are highly water-sensitive
- Acetylated starch is hydrophobic, but thermo-processed materials are brittle

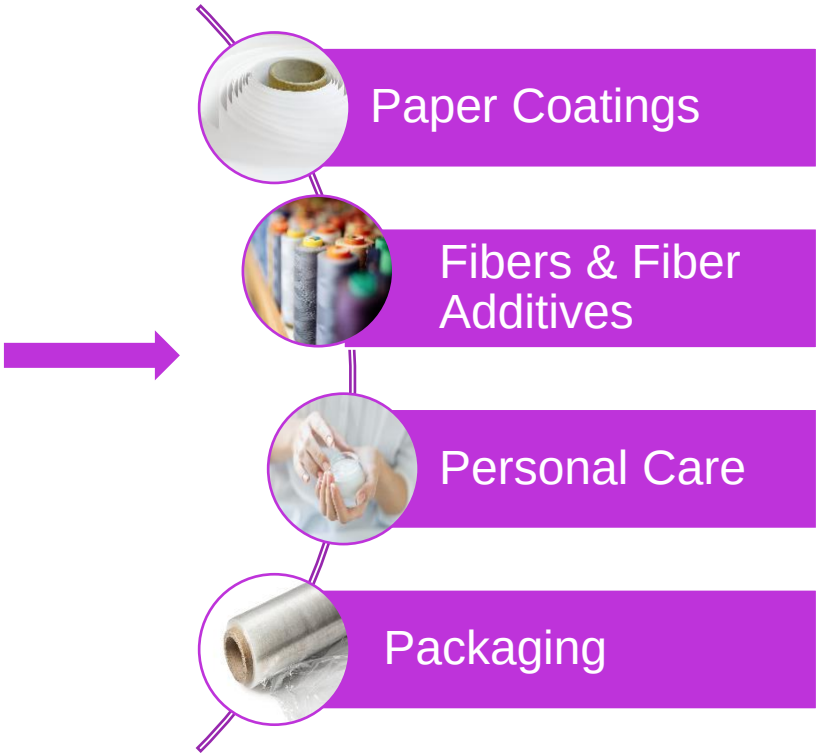
Starch Industrial Use



Starch: alpha (1,4) linkage

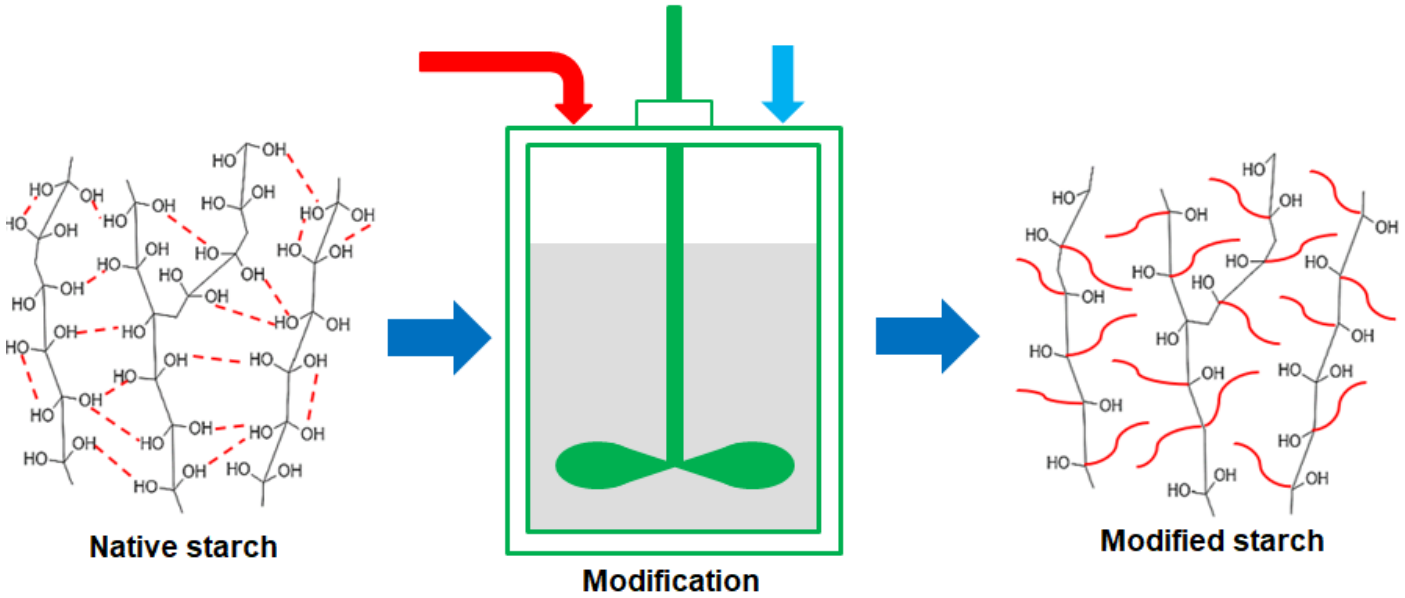


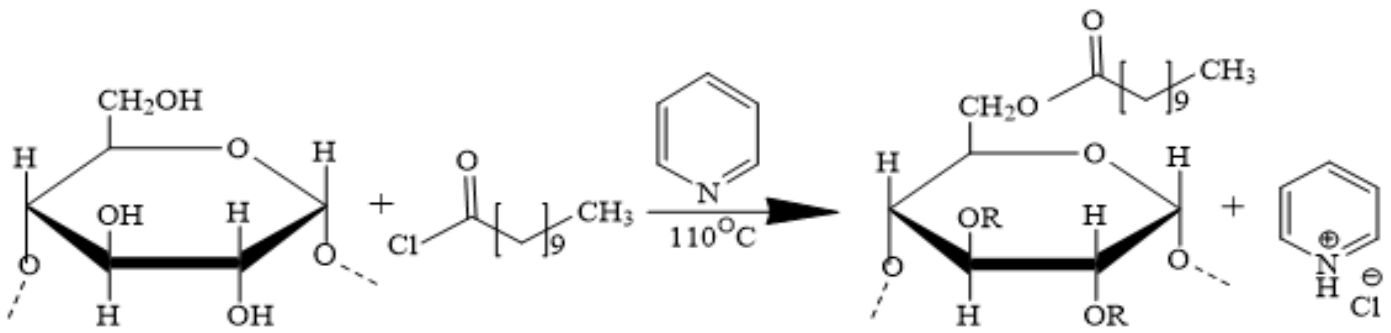
Industrail Applications of Starch



Starch modifications

- Typical modifications: thermoplastic processing





Experimental Methods

- Esterification reaction was carried out by dispersing starch in pyridine solvent and reacting with various mol ratios of starch/ lauroyl chloride at 110 ˚C and 1h

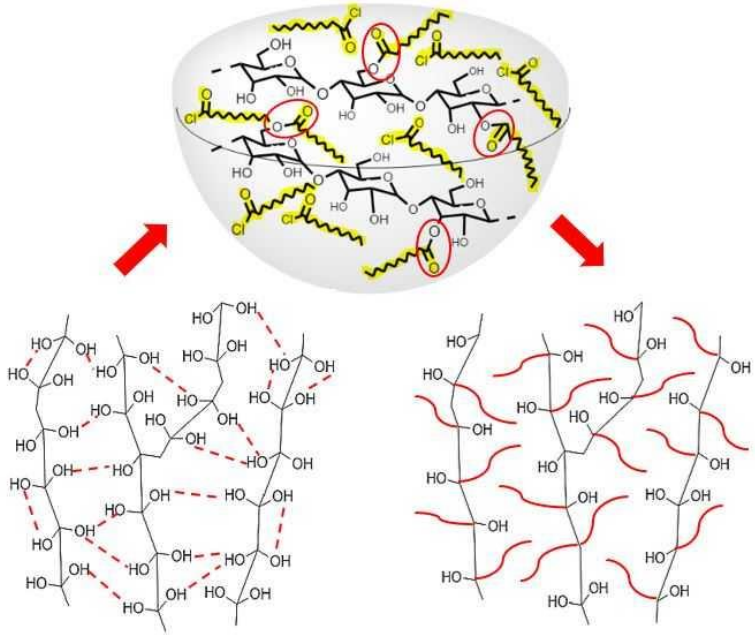
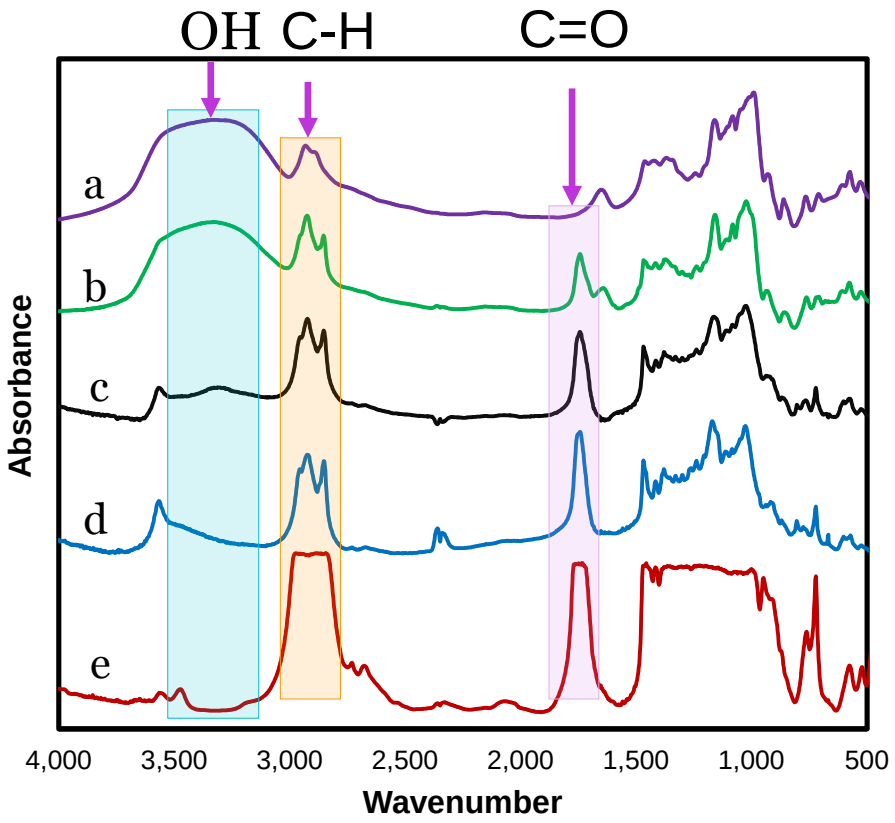


Figure 1. Experimental approach

Characterization Techniques

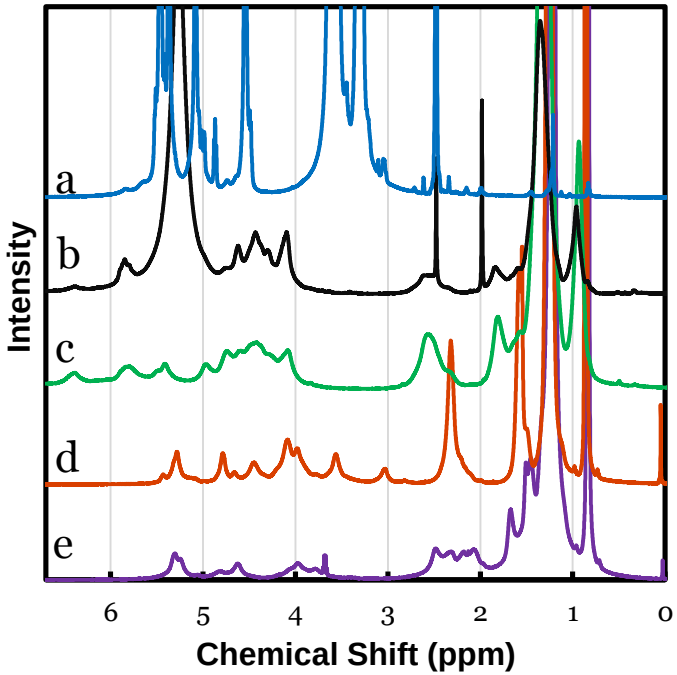
- Degree of substitution
  - Qualitative - FTIR
  - Quantitative - NMR and elemental analysis (EA)
- Thermal properties
  - Thermogravimetric analysis (TGA)
  - Differential Scanning Calorimetry (DSC)
- Morphology
  - Scanning Electron Microscopy (SEM)
  - X-ray diffraction (XRD)
- Hydrophobicity— Contact angle measurements

Degree of Substitution



FTIR (a) native starch, (b) DS 0.5, (c) DS 1.2, (d) DS 2.1 (e) DS 2.9

- Clear –OH reduction, and increase in methyl group.
- New peak at 1740 cm^{-1} - esterification (-C=O)



^{1}H NMR (a) native starch, (b) DS 0.5 (c) DS 1.2, (d) DS 2.1 (e) DS 2.9

- DS calculation using ^{1}HNMR

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Starch Esters

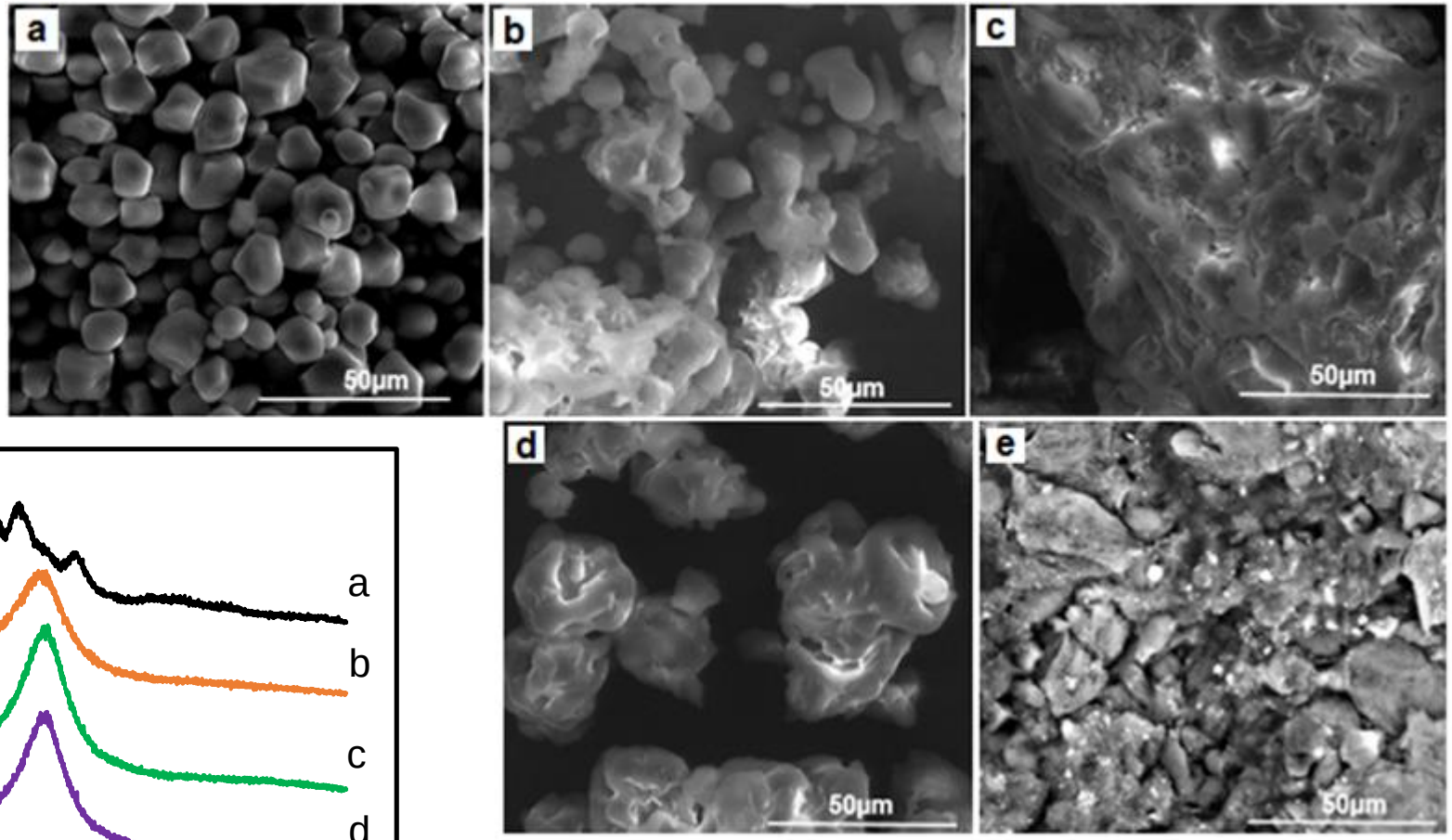
Table 1. Degree of substation by elemental analysis and nuclear magnetic resonance

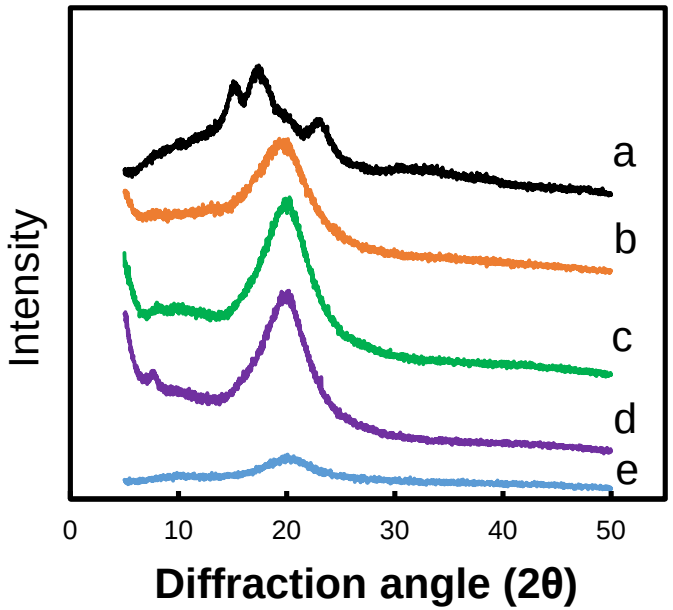
Mole Ratio	DS_{EA}	DS_{NMR}
1	0.47	0.44
1.5	1.21	1.31
2	2.1	1.96
4	2.88	2.92

EA – Elemental analysis

- With an increase in acid chloride concentration, high degree of substitution was achieved.

Morphology (SEM and XRD)

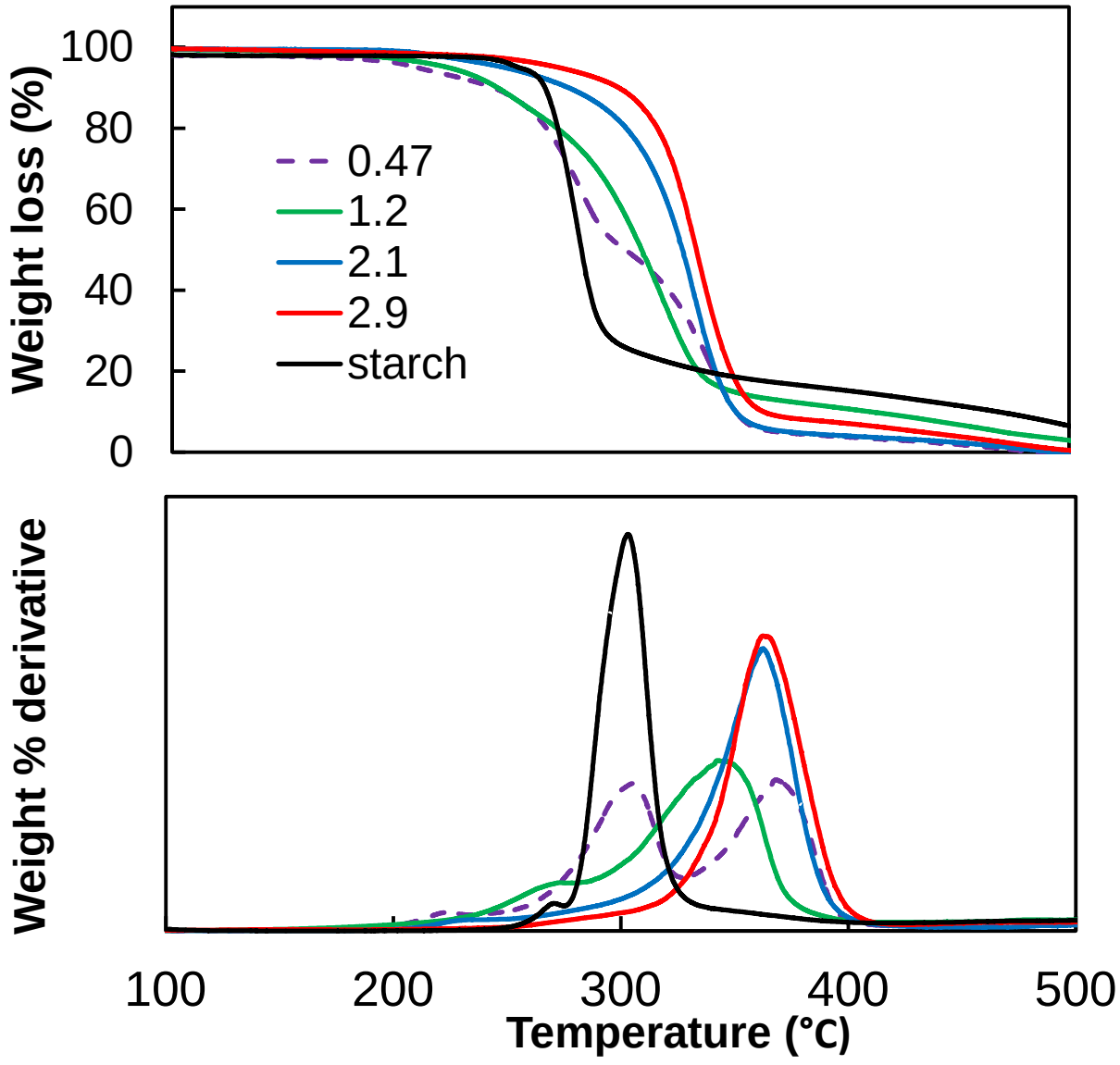




Clear morphology changes was observed

(a) Native starch, (b) DS 0.5, (c) DS 1.2, (d) DS 2.1, (e) DS 2.9

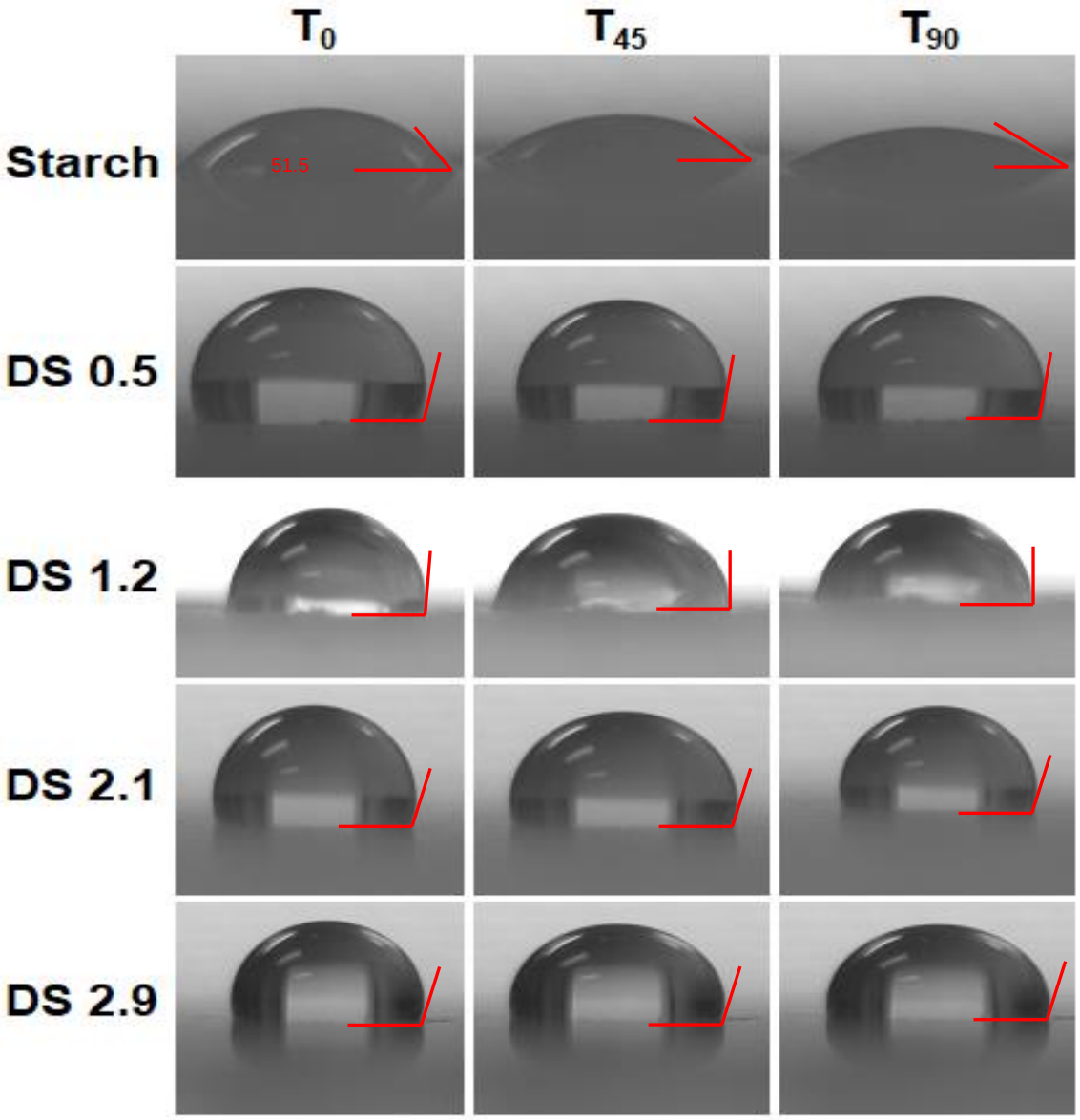
Thermal stability



- Overall thermal stability was improved.
- As the degree of modification increases, an increase in stability was noticed.

Figure 4.TGA thermograms of modified starch

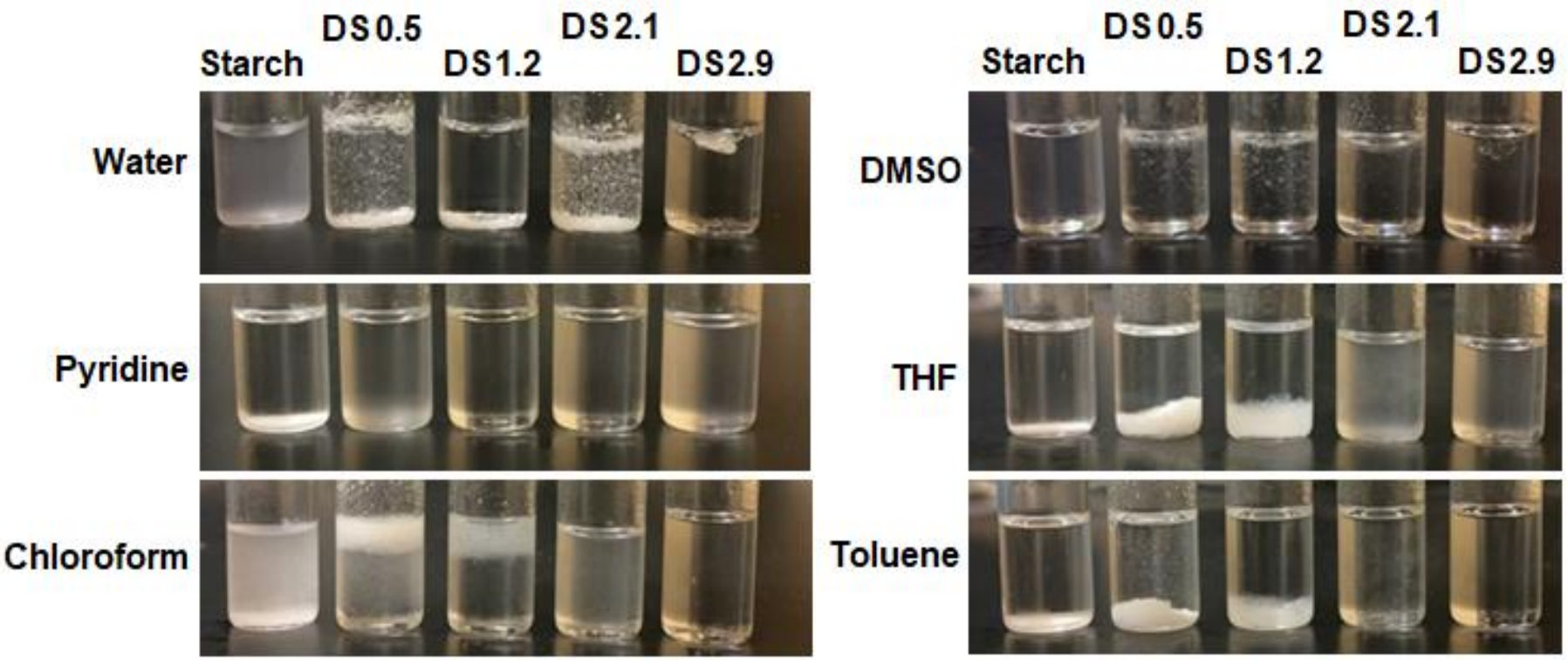
Hydrophobicity – contact angle measurement



- Surface wettability with time (0 – 90 seconds
- Modified starch films exhibited hydrophobicity

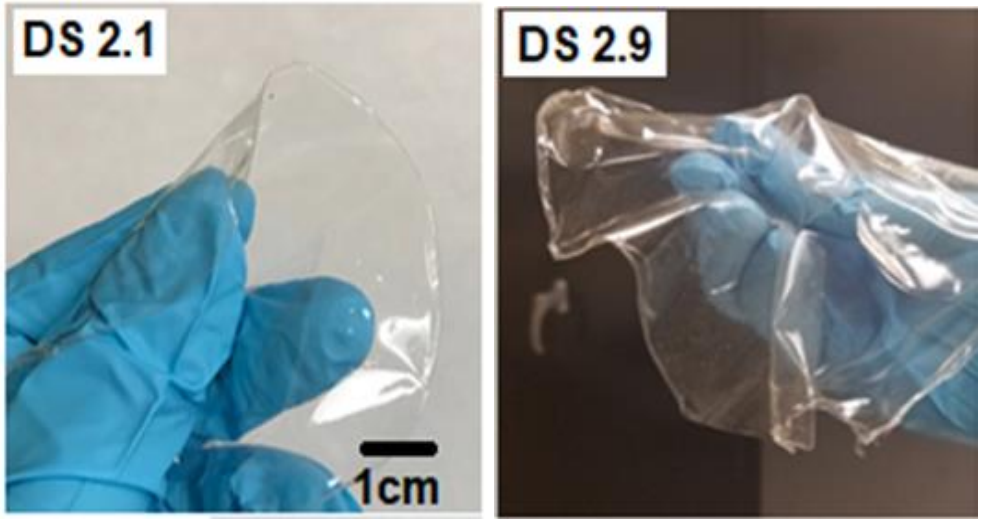
- An increasing trend of hydrophobicity with an increase in the DS of the starch

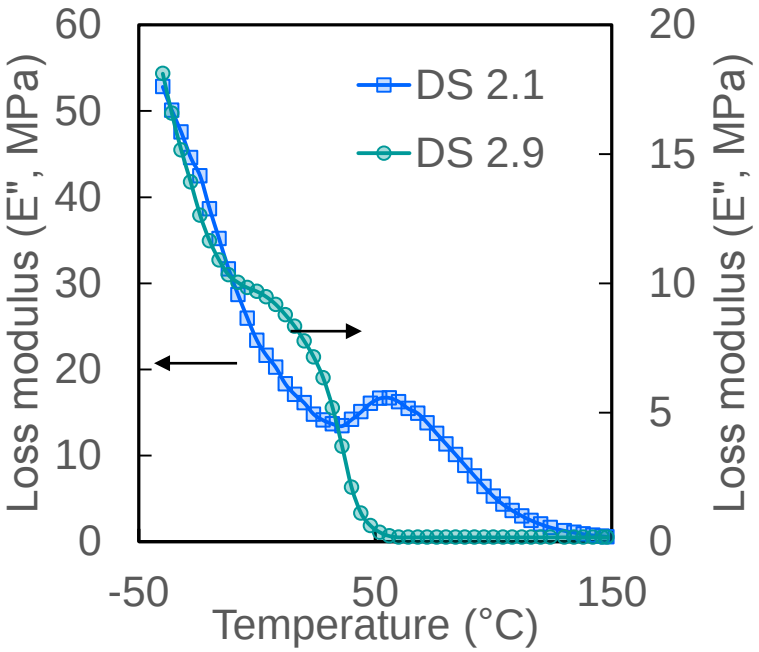
Hydrophobicity – solvent solubility

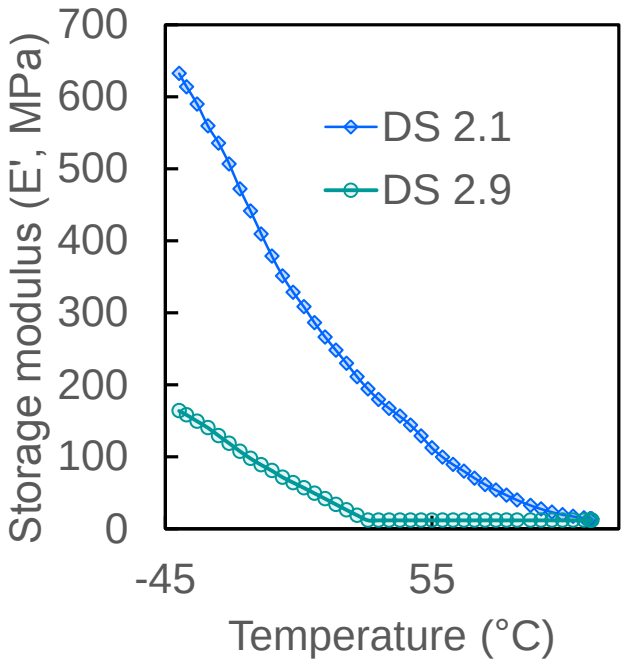


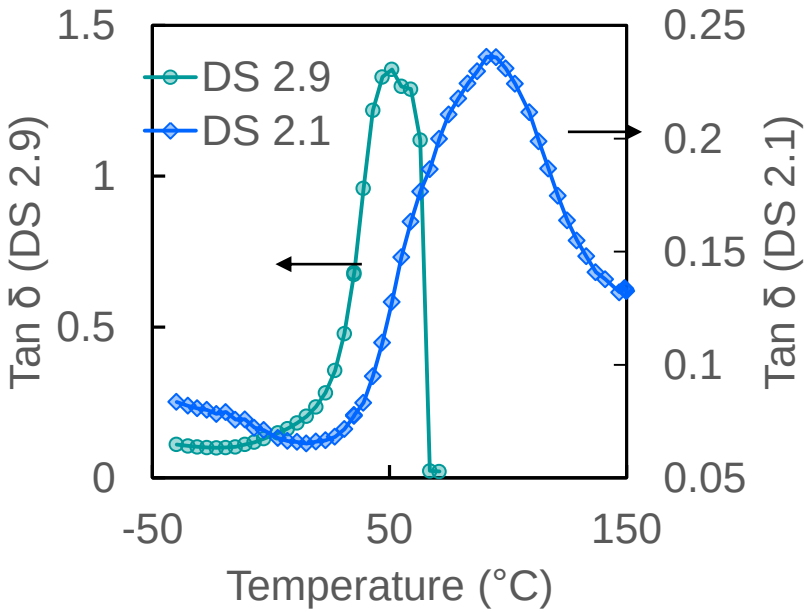
- Solubility behavior of polymers in solvents is essential to understand the solvent tolerance of the polymer.
- Change in solubility behavior of these polymers in various solvents illustrated the change in polarity of the modified starch

Dynamic Mechanical properties









Conclusions

- Successful esterification (EA and NMR results)
- Improved thermal stability
- Modified starch - melt processable
- Increased hydrophobicity

Future Work

- Further characterization and biodegradation study
- Investigate reactive extrusion process for similar modification
- Evaluate the performance of modified starch for hot melt adhesives, polymer blend systems and antimicrobial packaging applications

Thank you

Questions?