University of Waterloo

Polypropylene Modified Cellulose

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Outline

- **Introduction, Motivation**
  - Renewable Feedstock
  - Surface Modification of Wood Fiber
- **Objective of the Present Study**
  - Modify Surface of Wood Fiber to Improve Properties of Polypropylene
- **Results and Discussion**
  - Surface Modification of Wood Fiber
  - In-situ Polymerization of Propylene
  - Characterization of Materials
- **Conclusions**

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Faculty of Engineering

- about 260 faculty members
- over 1800 graduate students
- over 6340 undergrads
- undergraduate engineering program is Canada's largest and best
- co-operative education only
- branch in Dubai (since 2009, Chemical Eng. and Civil Eng., 1st and 2nd year)

Mike and Ophelia Lazaridis
Quantum-Nano Centre
(opening December 2011)

Engineering VI Building
Department of Chemical Engineering
(open now)

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Applications of Thermoplastic-Plant Fiber Composites

- Construction: flooring, decking, landscaping, roofing, furniture, windows and doors.
- Automotive: door panels, seats, bins, storage, battery tray…
- Packaging: pallets, trays, totes and boxes…

Quarter trim bin on Ford Flex using PP w/ 20-wt% wheat straw, material introduced in 2009. Developed in collaboration with University of Waterloo.

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Advantages of Plant Fibers (compared to glass fiber or mineral fillers)

- Renewable
- Lower density
- Relative low cost
- Biodegradable
- Excellent specific strength
- Easy to handle/work with

Disadvantages of Plant Fibers

- Hydrophilic nature
- Poor compatibility with non-polar matrix
- Poor dispersion of filler in PE and PP
- Absorb water
- Limited thermal stability

It is difficulty to obtain a good dispersion of wood fiber (micro size) in polypropylene using extrusion.

Impact strength decreases when wood fibers are added to polypropylene.

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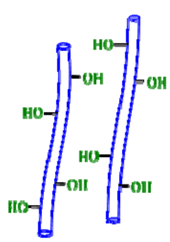
Highly hydrophilic nature → Hydrophobic nature



Wood Fiber

Possible Alternatives for Compatibilization with Polypropylene (PP)

- Surface modification of plant fiber
- Reactive extrusion (reactive groups between fiber-OH and polyolefin)
- Modification of polyolefin
- Use of compatibilizers (MA-PP, siline grafted PP)

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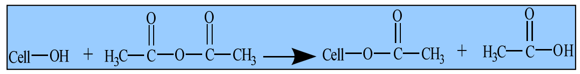
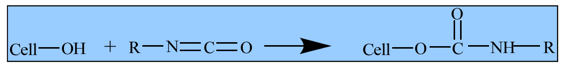
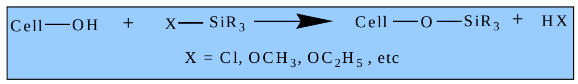
Alternatives for Surface Modification of Wood Fiber

- Acetylation
- Esterification
- Etherification
- Reaction with isocyanates
- Organo-silane treatment







These reactions involve utilization of -OH groups of wood fiber.

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Objective

- **To modify hydrophilic wood fiber to organophobic wood fiber, to allow a better dispersion in organic solvent.**
- **Conduct *in-situ* polymerization of propylene using the modified wood fiber.**
- **Compare properties of polypropylene with different methods for using the wood fiber.**

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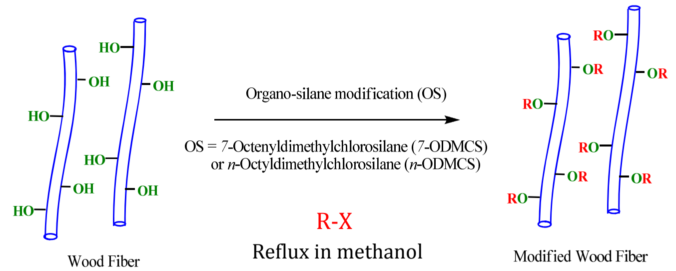
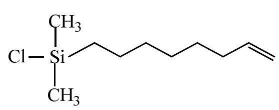
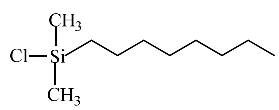
(1) Surface modification of wood fiber



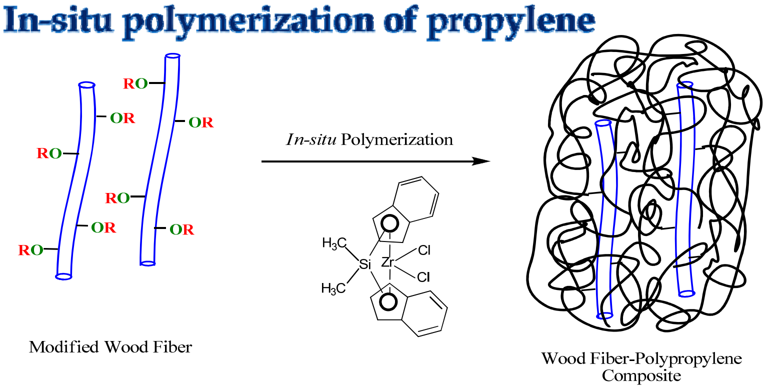


7-ODMCS



n-ODMCS

(2) In-situ polymerization of propylene



Co-catalyst: MAO

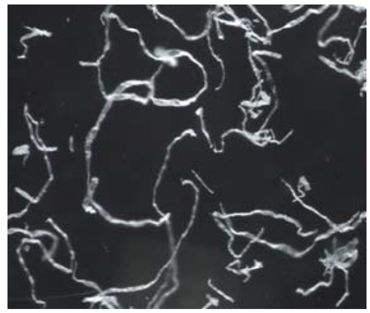
Solvent: Toluene

Temperature: r. t.

Catalyst: *rac*-dimethylsilylbis (1-indenyl)zirconium dichloride

Pressure: 20 psi

Wood Fiber



As received
(before modification)
- Obtained from pulp process
- Received in water

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Wood Fiber

Before modification

After modification

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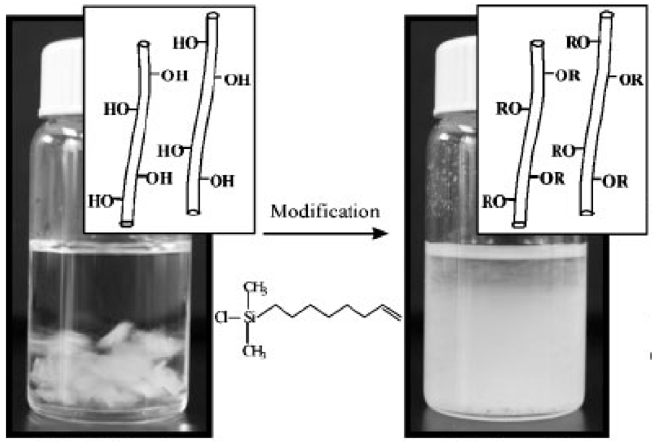

Wood Fiber in Toluene

Modified Wood Fiber in Toluene

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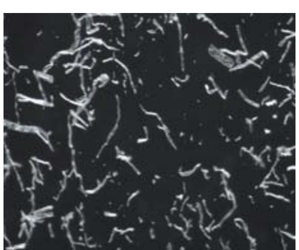
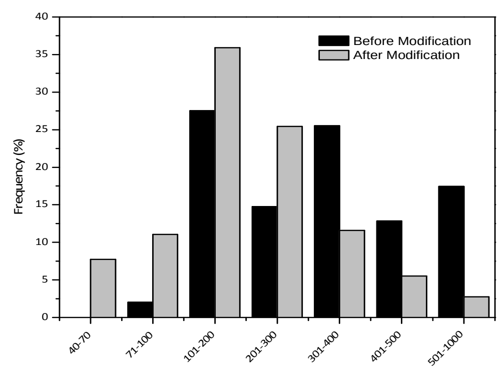
Particle Size Measurement

Un-modified Wood Fiber



Modified Wood Fiber



Before modification: most fibers have length 1-10mm

After modification: wide distribution 0.4-10mm (length reduced)

Diameter was almost same before and after modification (20-30 µm)

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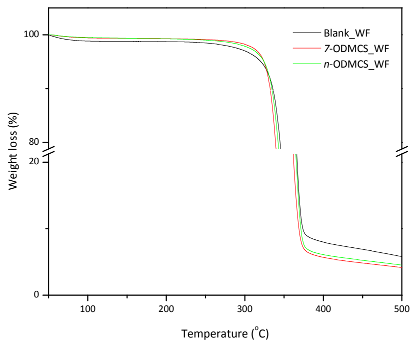
Thermal Stability of Wood Fiber



Sample	Weight loss between 200 and 400 °C (%)	Amount of silane grafted (mequiv./g)	Grafted yield (%)
Blank-WF	87.76	--	--
7-ODMCS_WF	93.65	0.37	7.4
n-ODMCS_WF	93.22	0.34	6.8

$$Grafted\ amount\ (m.equiv./g) = \frac{(W_{200} - W_{400}) \times 10^3}{[100 - (W_{200} - W_{400})] \times M} \qquad ...\ Equation\ (1)$$

$$Grafted\ yield\ (\%) = (Amount\ grafted/[Silane]) \times 100 \qquad ...Equation\ (2)$$

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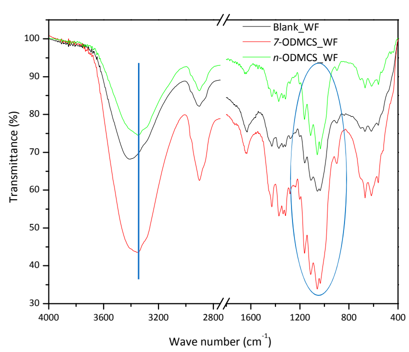
FT-IR spectra of Wood Fiber



Some changes in the IR spectra of modified fiber was noticed in 900-1200 cm^{-1} corresponding to Si-C, Si-O stretching.

However, the changes are not so prominent.

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In-situ Polymerization

Type of Modification	Fiber Content (g)	Reaction Time (min)	Polymer Yield (g)	Fiber (wt%)
Homo-polymerization	0.0	12	13.8	-
7-ODMCS_WF	1.0	25	12.5	8.0
n-ODMCS_WF	1.0	30	11.2	8.9

The reduced activity in presence of modified WF is due to deactivation of some catalyst by hydroxyl groups of fiber which were not reacted with silane modifier.

It is quite possible to decrease or increase the wood fiber content in final composite by varying reaction period or by varying the initial fiber loading.

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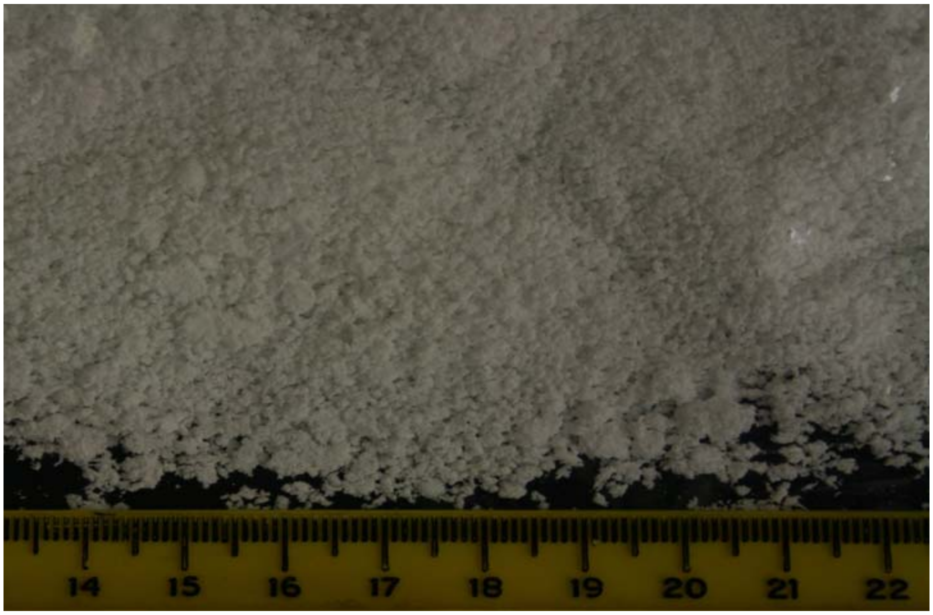

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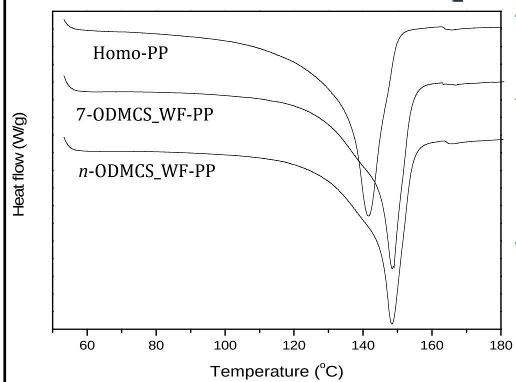
Thermal Analysis of WF-PP Composites



Sample	T_m (°C)	X_c (%)
Pure PP	139.0	27.27
n-ODMCS_WF-PP	145.0	27.34
7-ODMCS_WF-PP	145.3	28.83

Melt temperature and % crystallinity in case of WF-PP composites is higher than that of home PP.

DSC plots of WF-PP composites presents small shoulder at 135oC due to γ-crystal phase fusion.

Different insertion mechanism of propylene in presence of modified micro-cellulose

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Extraction of WF-PP

Sample	Fiber content (%)	Residue left on extraction (%)
Homo-PP	0	0
7-ODMCS_WF-PP	8.0	44
n-ODMCS_WF-PP	8.9	24

More amount of residue (44%) in case of olefin functionalized wood fiber is due to chemical bonding between fiber and polymer.

Lower amount of residue (24%) was also observed in case of WF modified with no olefin functionality.

The TiBA and MAO used during in-situ polymerization are reactive with hydroxyl groups of WF which in turns involved in polymerization with propylene leading to chemical bond b/w fiber and polymer.

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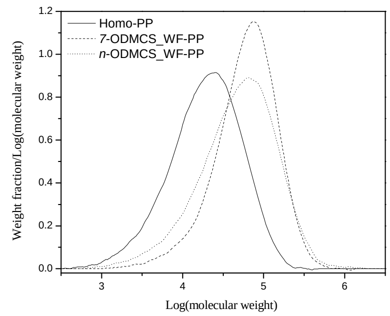
Molecular Weight of Polypropylene

Sample	M_n (g.mol^{-1})	M_w (g.mol^{-1})	PDI
Pure PP	10,431	29,369	2.8
7-ODMCS_WF-PP	36,192	82,477	2.3
n-ODMCS_WF-PP	22,939	80,374	3.5



- **Pure polypropylene showed lower molecular weight than the polypropylene obtained in presence of wood fiber.**
- **The polydispersity index for all samples are above the expected PDI = 2 for polypropylene produced by single site catalyst.**
- **The broader molecular weight distribution may have been caused by mass (monomer) or heat transfer limitations.**

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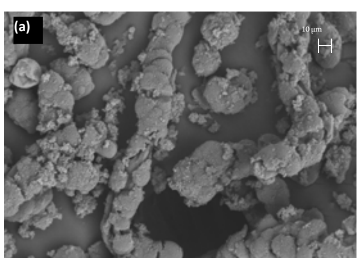
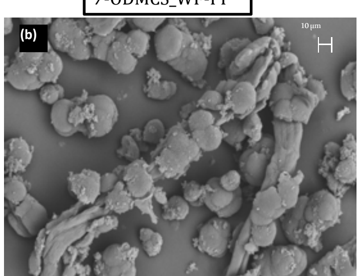
Morphology of Wood Fiber after Polymerization



7-ODMCS_WF-PP

Most fiber is covered with polymer

Vinyl groups are participating in co-polymerization with propylene



n-ODMCS_WF-PP

Incomplete coverage of fiber with polymer

No vinyl groups and hence no co-polymerization with propylene

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Conclusions

- Surface modification of wood fiber with organo-silane for polymerization is feasible
  - Good dispersion in organic solvent (toluene)
- Product of in situ polymerization suggests that polypropylene is bonded to the surface of wood fiber.
- Significant improvement in physical properties.

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