Recovery of Waste Polypropylene & Synthesis of a Sustainable Filament for Additive Manufacturing

Group 1:
Amanda Siciliano, Bryson Clifford,
Devorah Cahn, Benjamin Hudy-Velasco

Overview

- Motivation & Research Objective
- Polypropylene Fundamentals
- STRAP Method
- Additive Manufacturing
- Microcellulose Fundamentals
- Literature Review

Motivation & Research Objective

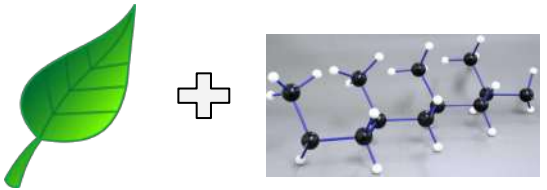
Motivation: Covid-19 global pandemic increased plastic pollution

- Estimated global demand of 129 billion face masks per month.[1]
- Additive manufacturing has a need for sustainable materials

Objective: Can we recycle and recover a single-use disposable waste source (i.e., Covid-19 masks) into an extrudable paste for additive manufacturing?

- **Aim 1:** *Recover* polypropylene (PP) from Covid-19 face mask waste using solvent-recovery techniques
- **Aim 2:** Use the recovered PP to *synthesize* a more sustainable extrudable polymer filament for additive manufacturing
- Use polymer physics fundamentals (i.e., crystalline structure, miscibility, phase separation, cohesive energy density, etc.)

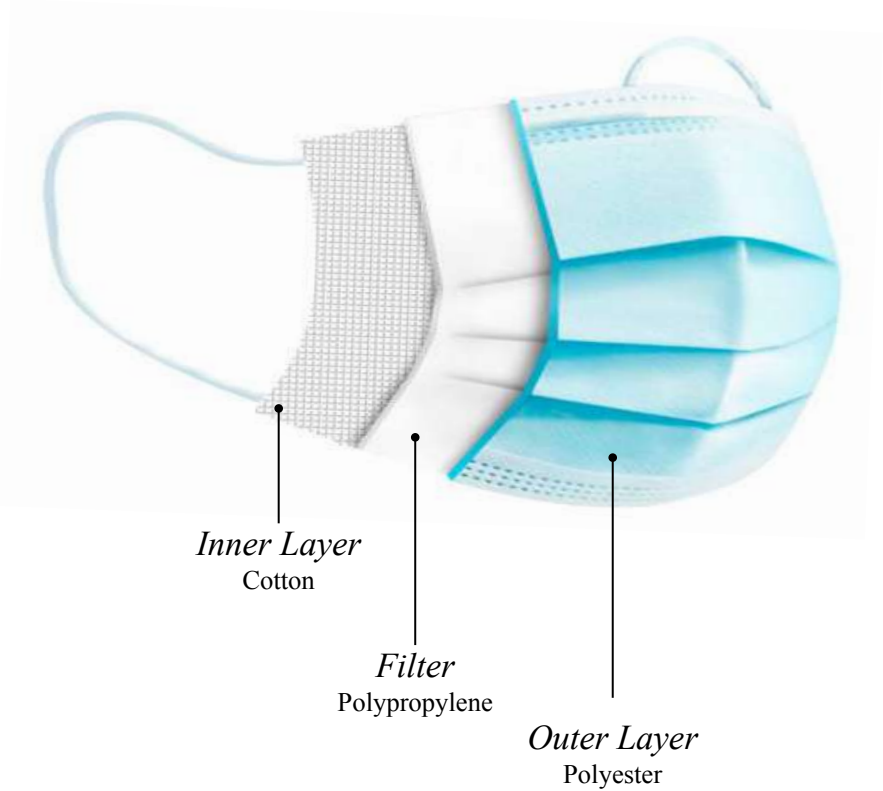
Aim 1:
Recovery



Aim 2:
Synthesis

[1] Prata, J. C. *Environ. Scie. Tech.*, vol. 54, no. 13, 2020.

COVID-19 Face Masks - Material Breakdown



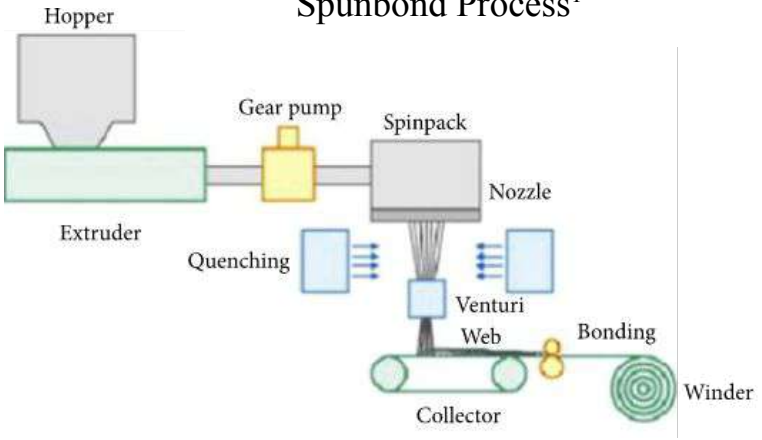
- Mask layers
  - Inner - Cotton
    - Hydrophilic
  - Filter - Polypropylene
    - Hydrophobic
  - Outer - Polyester
    - Hydrophobic
- Recoverable polypropylene (PP)[1]
  - N95 Mask - 11.5 g
  - Blue Disposable Surgical Mask - 4.5 g

[1] Abbasi, et al. *Saudi Journal of Biological Sciences*. 27.12. (2020).

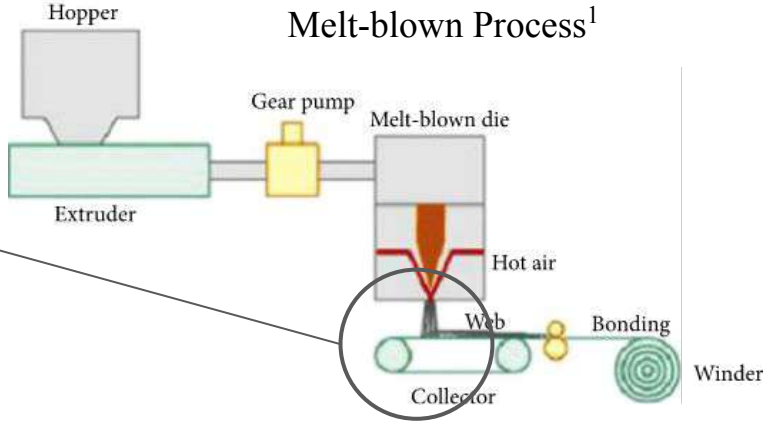
COVID-19 Face Masks - Fabrication

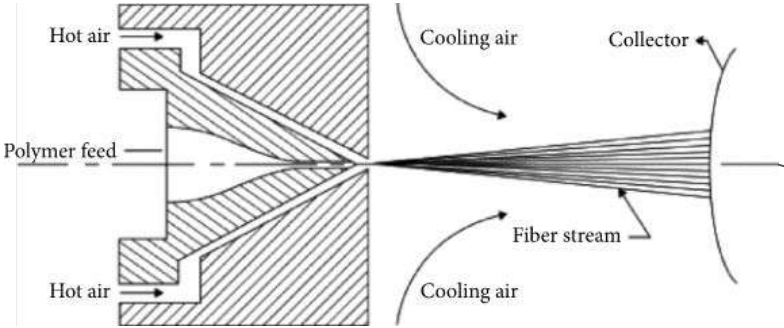
- Nonwovens - fabrics made by entangling fibers
- Nonwoven processes
  - Spunbond
  - Melt-blown

Spunbond Process[1]



Melt-blown Process[1]

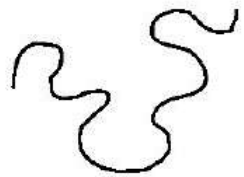




Meltblown Die-Assembly[2]

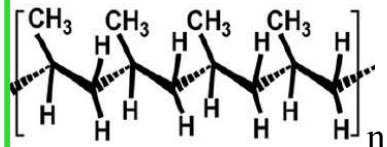
[1] Edwards, et al. *Thomas Net.* (2020).
[2] Hutten. *Handbook of Nonwoven Filter Media*. (2007).

Polypropylene (PP) Properties [1,2]

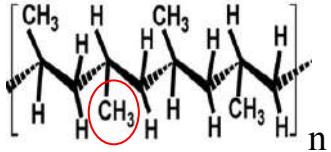


Linear architecture of thermoplastics

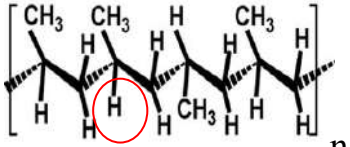
Isotactic



Syndiotactic



Atactic

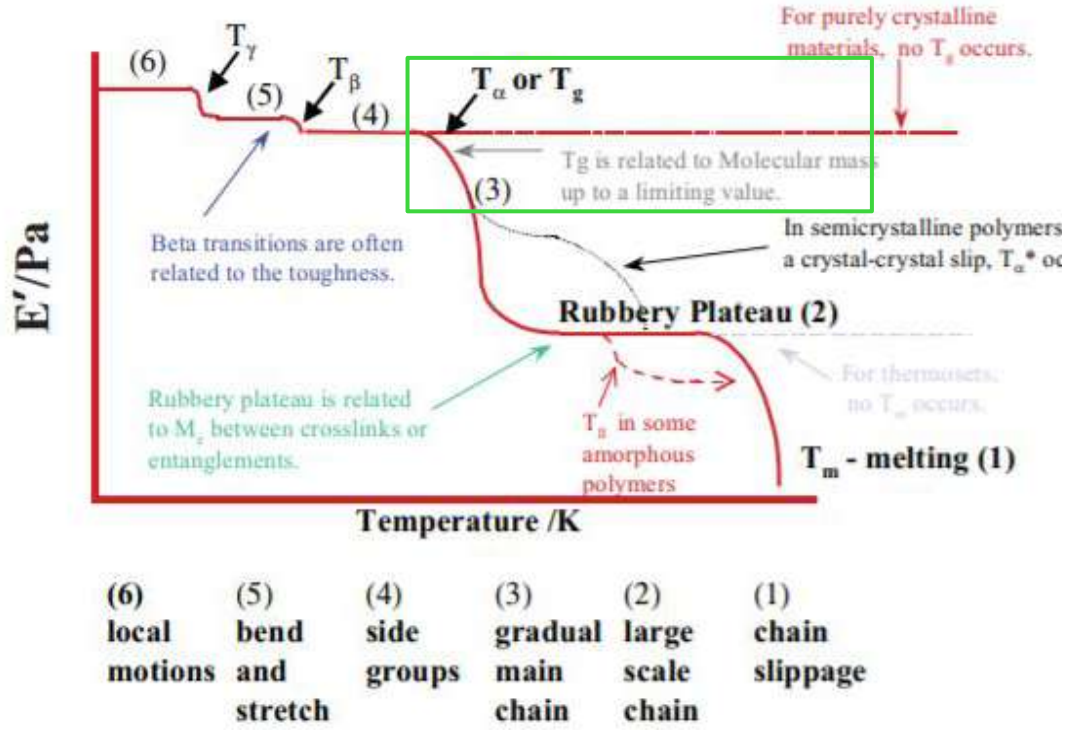


	Isotactic	Syndiotactic
Crystalline Structure	Monoclinic (α-structure)	Orthorhombic
Free Volume	Lowest	Medium
Melting Temperature	160-174°C	125-130°C
Glass Transition Temperature	Not found	Not found
Crystal Ratio	70-80%	~50%

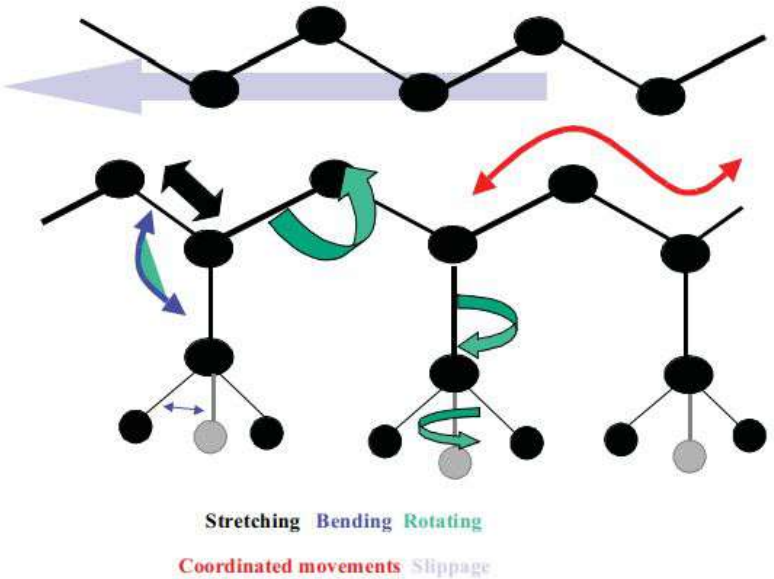
	Atactic
Crystalline Structure	Not applicable
Free Volume	Highest
Melting Temperature	Not applicable
Glass Transition Temperature	-17 -0 °C
Crystal Ratio	Not applicable

Isotactic Polypropylene is used in masks

[1] Hutten. *Handbook of Nonwoven Filter Media*. (2007).
[2] Rubenstein, et al. *Polymer Physics*. (2003).
[3] Natta, et al. "Crystalline Structure of Isotactic Polypropylene." 1967.



Types of Transitions [1]

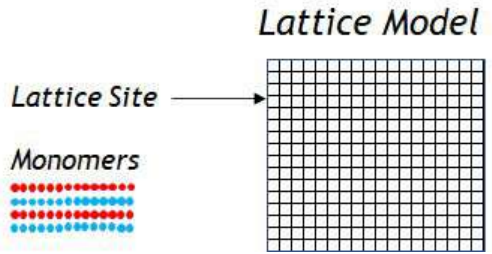


Crankshaft Model [1]

[1] PerkinElmer. *Technical Notes: Thermal Analysis.* (2007).

Flory Mean-Field Theory [1]

- **Model:** Lattice sites
- Lattice sites can be filled with
  - Monomers
  - Solvents
- No double occupancy
- Empty sites are filled
  - **<u>Ignores free volume</u>**
  - Assumes constant volume



Free Volume (FV) [1]

- Molecules in a liquid 'occupy' the majority of a liquid's volume. The remaining small fraction of the volume that is 'free' is used for molecular motion
- Relationships
  - As T ↑, FV ↑
  - As mobility ↑, FV ↑

[1] Rubenstein, et al. *Polymer Physics.* (2003).

Williams, Landel & Ferry (WLF) Equation [1]

- Describes temperature dependence of viscosity on polymer melts

η_0 = viscosity at reference temperature
B = empirical constant of order unity
f = fractional free volume
T_∞ = Vogel temperature

$$\frac{\eta}{\eta_0} = \exp\left(B\left[\frac{1}{f} - \frac{1}{f_0}\right]\right)$$

$$\frac{\eta}{\eta_0} = \exp\left(\frac{B}{\alpha_F}\left[\frac{1}{T - T_\infty} - \frac{1}{T_0 - T_\infty}\right]\right)$$

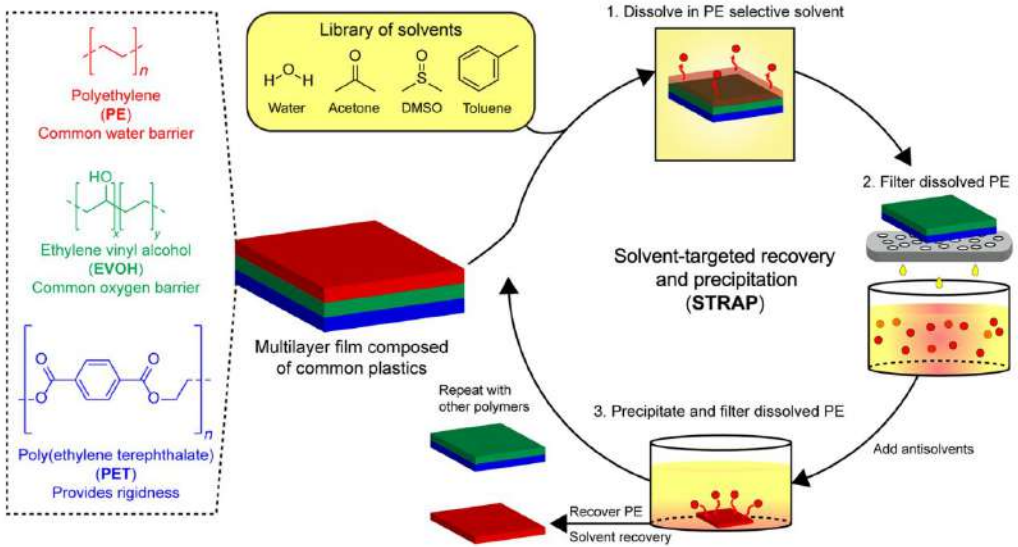
$$\frac{\eta}{\eta_0} = \exp\left(\frac{B}{\alpha_F}\left[\frac{T_0 - T}{(T - T_\infty)(T_0 - T_\infty)}\right]\right)$$

$$\frac{\eta}{\eta_0} = \exp\left(\frac{B}{f_0}\frac{(T_0 - T)}{(T - T_\infty)}\right)$$

[1] Rubenstein, et al. *Polymer Physics*. (2003).

Solvent-targeted Recovery & Precipitation (STRAP) Method

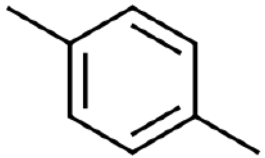
- Use solvent to selectively dissolve one polymer
  - Only polymer in that layer is soluble in the solvent
- Use filtering & poor solvent to precipitate & recover the soluble polymer
- Use different solvent to target & recover material in next layer
- Utilize Hansen solubility parameters, molecular dynamics, and COSMO-RS



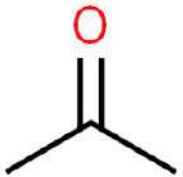
[1] Walker et al. Science Advances. (2020).

Solvent Properties

- Good Solvent:
  - Maximize entropy
  - Minimize Gibbs/Helmholtz free energy of mixing
    - **Miscible**
  - PP requires nonpolar solvents such as xylene
- What makes a poor solvent:
  - Positive Gibbs/Helmholtz free energy of mixing
    - **Immiscible**
  - Polymer molecules prefer to interact with themselves than the solvent
  - PP precipitation requires a (polar) poor solvent such as acetone



Xylene (good PP solvent)



Acetone (poor PP solvent)

[1] Rubenstein, et al. *Polymer Physics.* (2003).
[2] Poulakis & Papaspyrides. Resources, Conservation, and Recycling. (1997).

Thermodynamics of Mixing

Entropy

- $S = k \ln \Omega$
  - k = Boltzmann constant
  - Ω = degrees of freedom
- $$\Delta \bar{S}_{mix} = -k \left[\frac{\phi_{PP}}{N_{PP}} \ln \phi_{PP} + \phi_{Solvent} \ln \phi_{Solvent} \right]$$
  - ϕ = volume fraction
  - N = number of occupied lattice sites

Energy of Mixing

- $$\Delta \bar{U}_{mix} = \chi \phi (1 - \phi) kT$$
  - *Flory Interaction Parameter:* $$\chi \equiv \frac{z}{2} \frac{\left(2u_{PP\_Solvent} - 2u_{PP\_PP} - u_{solvent\_solvent}\right)}{kT}$$

Helmholtz Free Energy (Flory-Huggins Equation)

- $$\Delta \bar{F}_{mix} = kT \left[\frac{\phi}{N} \ln \phi + (1 - \phi) \ln(1 - \phi) + \chi \phi (1 - \phi) \right]$$

[1] Rubenstein, et al. *Polymer Physics.* (2003).

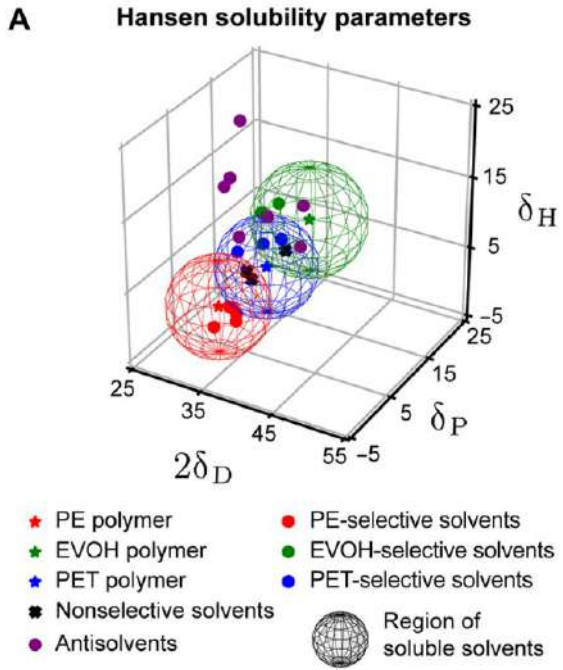
Solubility Parameters

- Hansen solubility parameters
  - δD: Dispersion (van der Waals)
  - δP: Polarity (related to dipole moment)
  - δH: hydrogen bonding
  - Compares distance between parameters for polymer and solvents (closer distance = better solvent):

$$Ra^2 = 4(\delta D_1 - \delta D_2)^2 - (\delta P_1 - \delta P_2)^2 - (\delta H_1 - \delta H_2)^2$$

  - For PP ($MPa^{1/2}$): δD = 18.0, δP = 0, δH = 0
- Hildebrand/Scott solubility parameter

$$\delta \equiv \sqrt{\frac{\Delta E_{PP}}{v_{PP}}} \quad \rightarrow \quad \chi \approx \frac{v_0}{kT}(\delta_{PP} - \delta_{Solvent})^2$$



[1] https://www.hansen-solubility.com/HSP-science/basics.php
[2] Walker et al. Science Advances (Vol. 6, no. 47). 2020.
[3] Rubenstein, et al. *Polymer Physics.* (2003).

Calculating the Solubility Parameter

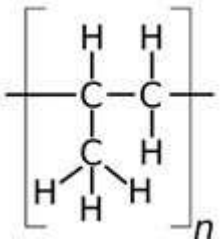
- Solubility can be calculated based on group contributions from functional groups:

$$\delta = \frac{\sum_i F_i^*}{\sum_i V_i^*}$$

  - F_i^* = molar attraction constant for *i*th group
  - V_i^* = molar volume constant for *i*th group
- To calculate the solubility parameter for polypropylene:

(218 + 132 + 23) / (31.8 + 16.5 + 1.9) =

7.43 $(cal.cm^{-3})^{0.5}$



Group	Molar Attraction Constant (F^*, $(cal.cm^3)^{0.5}mole^{-1}$)	Molar Volume Constant (V^*, $cm^3\ mole^{-1}$)
CH_3	218	31.8
$-CH_2-$	132	16.5
>CH-	23	1.9

[1] Painter & Coleman. Essentials of Polymer Science and Engineering. 2008.

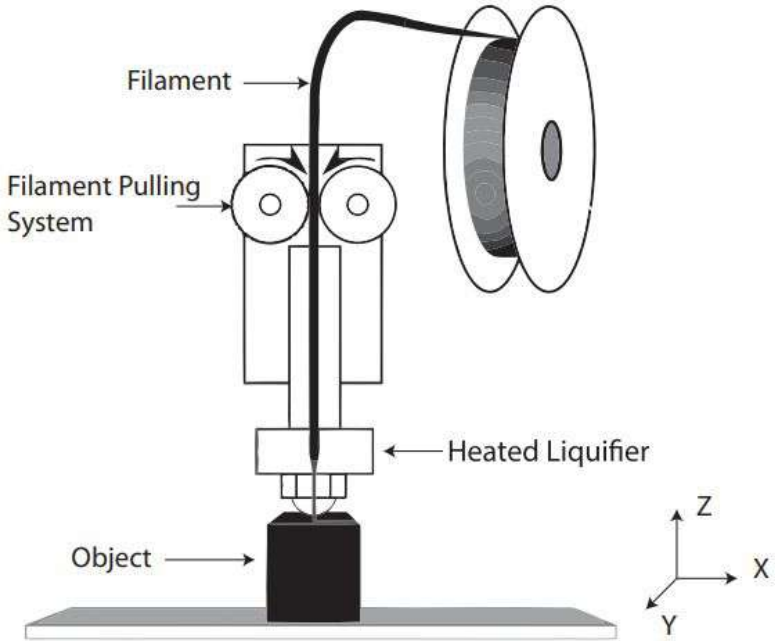
Additive Manufacturing

- **Material Deposition Processes**
  - **Extrusion Process**
    - **Thermoplastics**
    - **Elastomers**
    - **Graphite**
    - **Metals**
    - **Other***
  - Blown Powder Process
    - Metals
  - Cold Spray
    - Metals
- Powder Bed Processes
  - Laser Melting (LM)
    - Metals
  - Laser Sinter (LS)
    - Metals
    - Thermoplastic
    - Elastomers
    - Ceramics
    - Other*
  - Binder Jet
    - Metals
    - Thermoplastic
    - Elastomers
    - Ceramics
    - Other*
- Liquid Bed Processes
  - Electron Beam Melting (EBM)
    - Non-Ferrous Alloys
  - Stereo-lithography
    - Thermosetting Resin

*Can print anything that melts and then hardens

*Can print anything that is in powder form

Fused Deposition Modeling (FDM)



Makerbot

- high-quality polymers like ABS, Nylon, Nylon Carbon Fiber, PC-ABS, ASA, PETG, SR-30, PVA, and more.

[1] Carneiro, O. S., et al. *Materials & Design*, vol. 83, 2015.

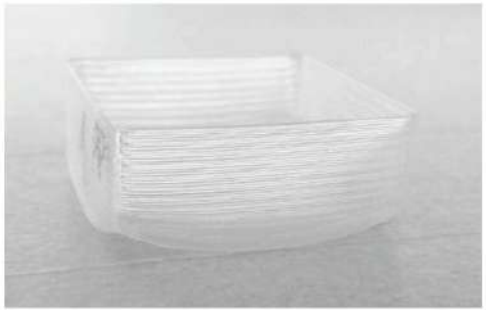
FDM Printing Challenges with PP

- Larger shrinkage than other polymer filaments (i.e., ABS, PLA, PETG)
  - Crystallization causes decrease in volume
  - Higher shrinkage for lower cooling rates
- Poor bed adhesion
- Lost production time (to deal with issues)
- Thus, PP is not widely used in 3D Printing

Material	**Linear Coefficient of Thermal Expansion (10^{-5}/°C)**
ABS[1]	7-15
PLA[1]	8.5
PP[1]	7-17
Cellulose Fiber	1-18

Our Solution: include a filler to the PP matrix to modify its physical properties

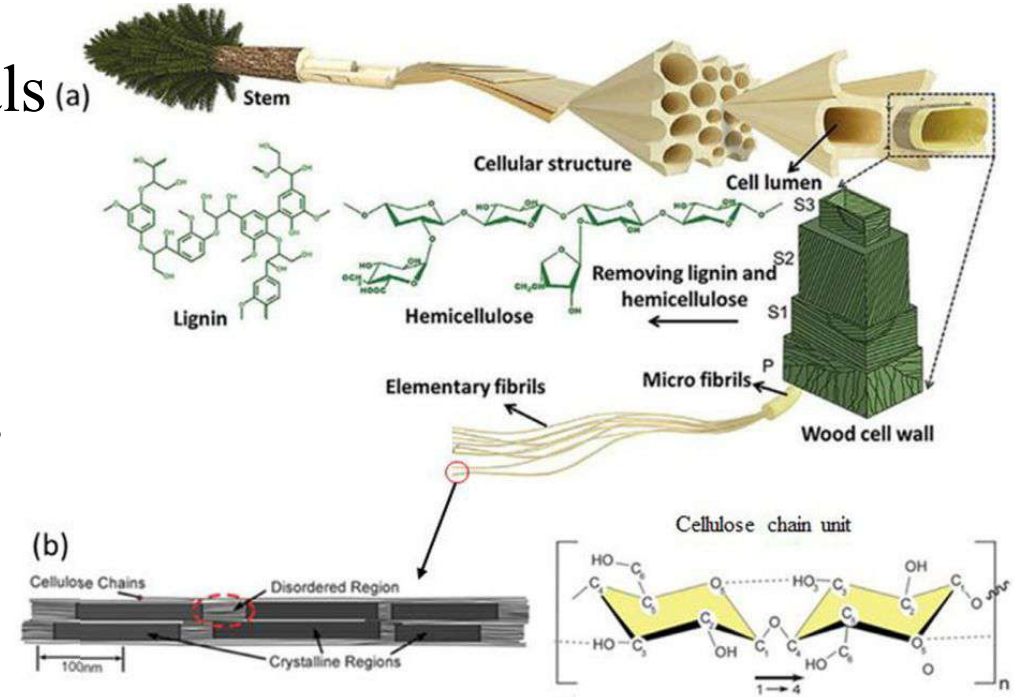
- Natural fiber filler (green/sustainable material)



Structure manufactured with fused deposition modeling of polypropylene showing shrinkage after printing.[2]

[1] SpecialChem SA. 2021.
[2] Carneiro, O. S., et al. *Materials & Design*, vol. 83, 2015.

Microcellulose Fundamentals



Benefits for thermoplastic polymers

- Highly available (agricultural waste)
- High specific mechanical properties
  - Can be modified by grafting of polymers and other functional groups onto cellulose surface
- **Creates genuine sustainability**

Uses of cellulose in additive manufacturing:

- Improve interfacial adhesion
- Matrix reinforcement
- Rheology modifier
- Improve thermal stability

Cellulose fibers are classified by their structure and morphology:

Microcrystalline cellulose (MCC)
Cellulose microfibre (MF):
Nanofibrillated cellulose (NFC)
Cellulose nanocrystal (CNC)
Bacterial cellulose particles (BC)
Regenerated cellulose (RC):

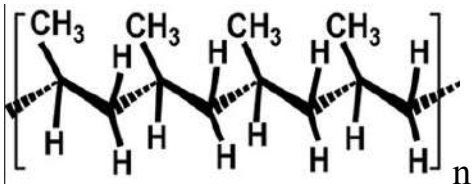
[1] Gauss et al. *J. Composites Part C.* (**2021**)

Incompatibility of PP + Cellulose Polymer

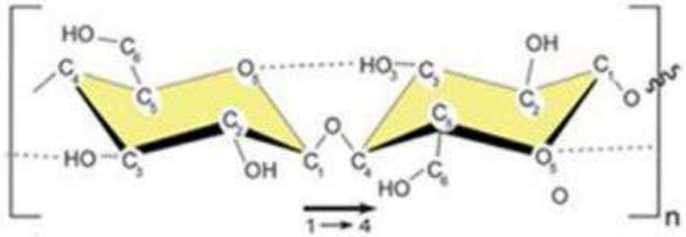
Challenge: *Nonpolar*, *hydrophobic* PP does not readily mix with *polar*, *hydrophilic* cellulose fibers (we expect phase separation due to decreased entropy after mixing)

$$\Delta \bar{S}_{mix} = -k\left[\frac{\varphi_{PP}}{N_{PP}}\ln(\varphi_{PP}) + \frac{\varphi_{cellulose}}{N_{cellulose}}\ln(\varphi_{cellulose})\right]$$

Isotactic PP



Cellulose chain unit



[1] Rubenstein, et al. *Polymer Physics*. (2003).
[2] Gauss et al. *J. Composites Part C.* (**2021**).

Incompatibility of PP + Cellulose Polymer

Hydrophobic-hydrophilic
Polar-nonpolar

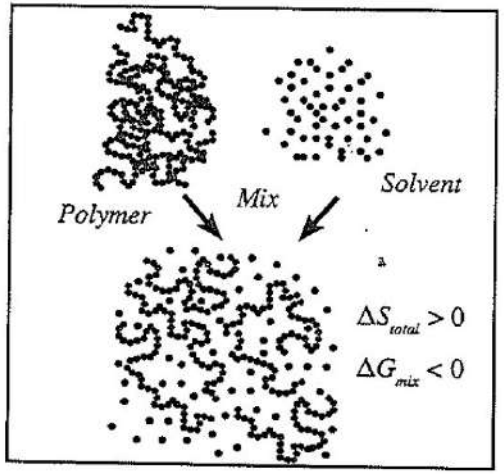
Solutions:

1) *Chemical surface treatment*
   a) Mercerization (NaOH (aq)) → exposes OH groups on the cellulose surface to increase reactive sites & clean surface
   b) Esterification → OH groups (hydrophilic) transformed into ester bonds (hydrophobic), improving the natural fiber-PP matrix compatibility
2) *Covalently graft* maleic anhydride (MA) to the PP matrix to create maleated PP (MAPP)
   a) MA group on the MAPP matrix can now react with the OH group on the fiber surface

[1] Zhang et al. *Green Energy and Technology*, (2017)

(1) Chemical Surface Treatment

Alkoxide



Swelling of polymer in good solvent

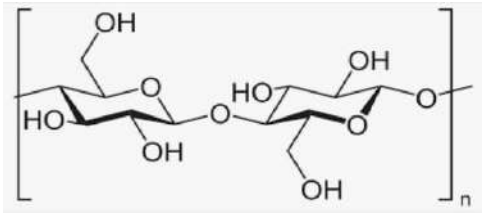
Step a): *Alkaline chemical surface treatment*

- Cellulose swells in NaOH solvent to expose more reactive sites
- Alkoxide is converted back to OH sites with a water wash
- Purpose: Increases reactive sites ("amorphousness"), cleans surface

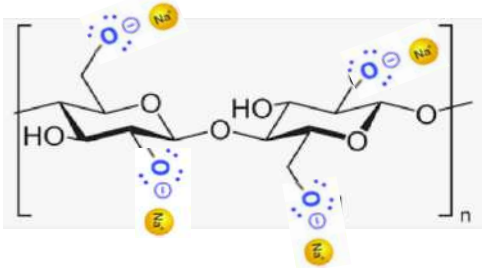
,

,

NaOH aqueous

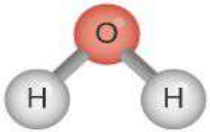


Cellulose monomer with hydroxyl groups



Cellulose monomer with alkoxide groups

,



Water

, Impurities

[1] Zhang et al. *Green Energy and Technology*, (**2017**)

[2] Painter et al. *Essentials of Polymer Science and Engineering*, (**2009**)

(1) Chemical Surface Treatment

$$\chi = \frac{z\Delta\varepsilon_{AB}}{kT}$$

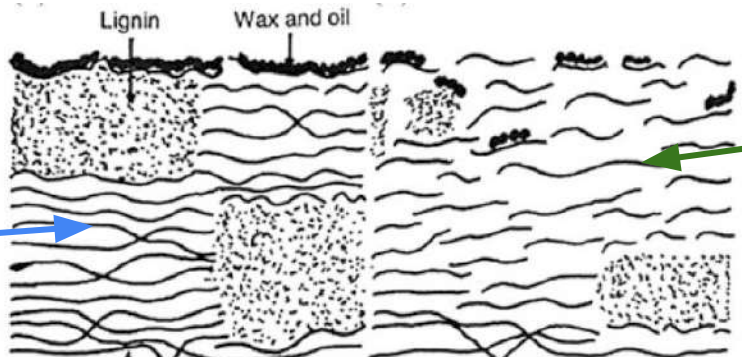
EQUATION 11-25

$$\frac{\Delta G_m}{RT} = n_A \ln \Phi_A + n_B \ln \Phi_B + n_A \Phi_B \chi$$

EQUATION 11-28

Step b): *Esterification*

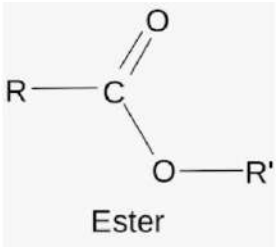
- Cellulose (with lots of OH groups) swells in acetic acid solvent, then reacted with acetic anhydride at high temp.
  - Acetylating agents more likely to react with OH groups in amorphous regions (i.e. lignin, hemicellulose) because *diffusion is difficult in high crystalline regions* (i.e. cellulose)
- Purpose: OH (hydrophilic) converted to ester (*more* hydrophobic) so more compatible with PP



High crystalline cellulose

More amorphous cellulose

BEFORE alkaline treatment AFTER alkaline treatment



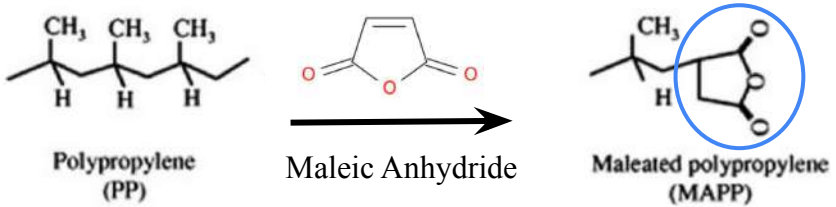
Ester

[1] Zhang et al. *Green Energy and Technology*, (**2017**) [2] Painter et al. *Essentials of Polymer Science and Engineering*, (**2009**)

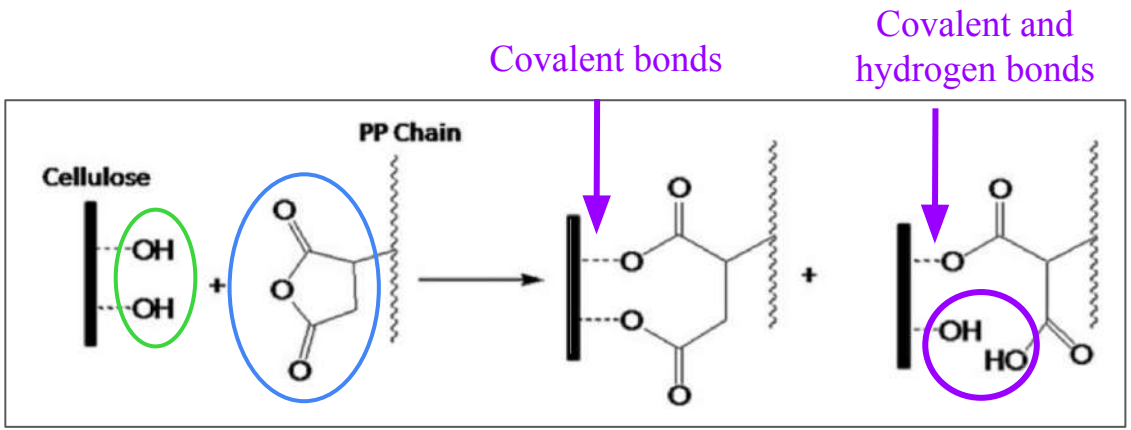
(2) Covalent Grafting

Polar - Non-Polar

a) *Covalently* graft MA onto PP



b) MA groups on PP will then react with the OH groups on cellulose polymer via *covalent* bonds



- *Surface energy* of cellulose decreases, improving the interfacial adhesion between natural polymer and PP matrix

[1] Zhang et al. *Green Energy and Technology*, (**2017**)

[2] Painter et al. *Essentials of Polymer Science and Engineering*, (**2009**)

Surface Energy - Free Energy of Mixing Relationship

- *Surface energy* ⇔ cohesive energy density (CED) ⇔ solubility parameter (energy of vaporization)

Hildebrand:

$$\delta_A = C_{AA}^{0.5} \qquad \delta_B = C_{BB}^{0.5}$$

EQUATIONS 11-32

$$\Delta H_m = (n_A + n_B) V_m \Phi_A \Phi_B (\delta_A - \delta_B)^2$$

EQUATION 11-33

Flory:

$$\Delta G_m = \Delta H_m - T\Delta S_m$$

Polymer or Blend	Solubility Parameter* $(Cal/cm^3)^{1/2}$	CED (Cal/cm^3)
PP	7.43	55.20
MAPP	9.32	86.86
Cellulose	12.07	145.68
MA-Cellulose	12.30	151.30
Cellulose-MAPP	11.12 (average)	123.65 (average)

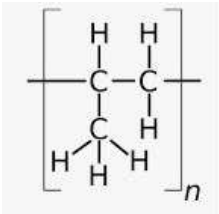
*calculated using Group Contributions Method

[1] Painter et al. *Essentials of Polymer Science and Engineering*, (**2009**)

Solubility Parameter Calculation

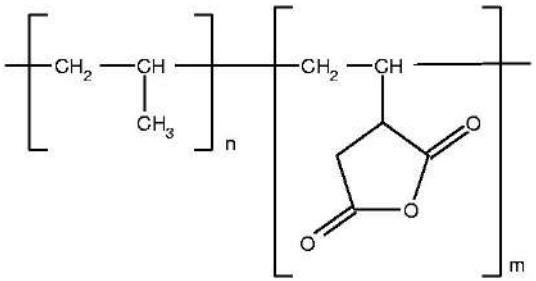
- Group Contribution Method
  - Functional groups influence the energy of vaporization of the overall polymer

Polypropylene (PP)



$$\delta_{PP} = \frac{218 + 132 + 23}{31.8 + 16.5 + 1.9} = 7.43 \left(\frac{cal.}{cm^3}\right)^{0.5}$$

Maleated Polypropylene (MAPP)



$$\delta_{MAPP} = \frac{218 + 3(132) + 3(23) + 95 + 2(18)}{31.8 + 3(16.5) + 3(1.9) + 5.1 + 2(-2.4)} = 9.32 \left(\frac{cal.}{cm^3}\right)^{0.5}$$

$$\delta = \frac{\sum_i F_i}{\sum_i V_i} (cal.\ cm^{-3})^{0.5}$$

EQUATION 11-38

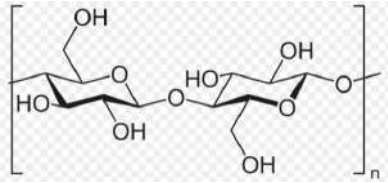
TABLE 11-1 GROUP CONTRIBUTIONS

GROUP	MOLAR VOLUME CONSTANT V^* ($cm^3\ mole^{-1}$)	MOLAR ATTRACTION CONSTANT F^* [$(cal.\ cm^3)^{0.5}\ mole^{-1}$]
$-CH_3$	31.8	218
$-CH_2-$	16.5	132
$>CH-$	1.9	23
$>C<$	−14.8	−97
$>C_6H_3-$	41.4	562
$-C_6H_4-$	58.5	652
C_6H_5-	75.5	735
$CH_2=$	29.7	203
$-CH=$	13.7	113
$>C=$	−2.4	18
$-OCO-$	19.6	298
$-CO-$	10.7	262
$-O-$	5.1	95
$-Cl$	23.9	264
$-CN$	23.6	426
$-NH_2$	18.6	275
$>NH$	8.5	143
$>N-$	-5.0	-3

[1] Painter et al. *Essentials of Polymer Science and Engineering*, (**2009**)

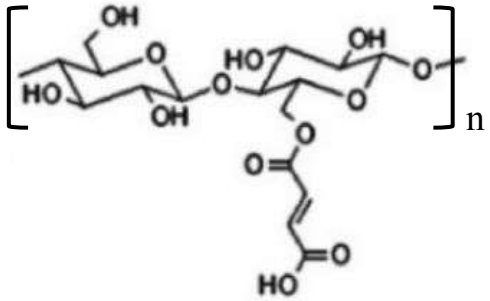
Solubility Parameter Calculation

Cellulose



$$\delta_{Cellulose} = \frac{2(132) + 10(23) + 4(95)}{2(16.5) + 10(1.9) + 4(5.1)} = 12.07 \left(\frac{cal.}{cm^3}\right)^{0.5}$$

MA-Cellulose



$$\delta_{MA-Cellulose} = \frac{2(132) + 10(23) + 5(95) + 2(18) + 2(113)}{2(16.5) + 10(1.9) + 5(5.1) - 2(2.4) + 2(13.7)} = 12.30 \left(\frac{cal.}{cm^3}\right)^{0.5}$$

$$\delta = \frac{\sum_i F_i}{\sum_i V_i} (cal.\ cm^{-3})^{0.5}$$

EQUATION 11-38

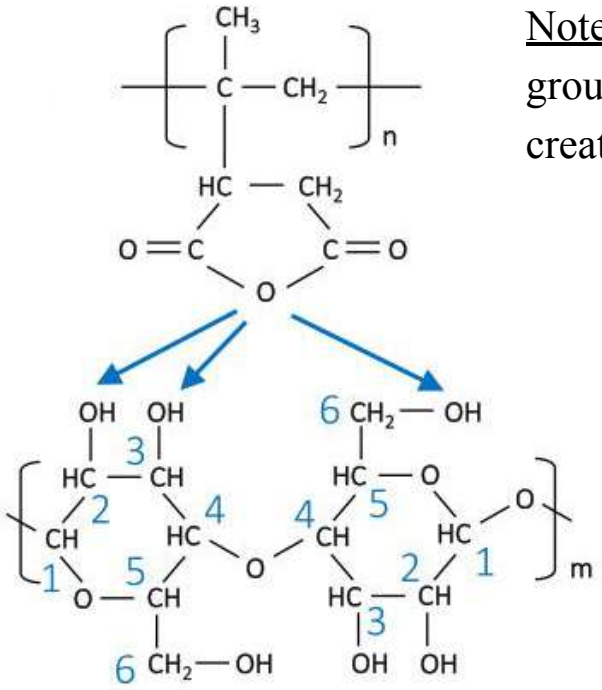
TABLE 11-1 GROUP CONTRIBUTIONS

GROUP	MOLAR VOLUME CONSTANT V^* ($cm^3\ mole^{-1}$)	MOLAR ATTRACTION CONSTANT F^* [$(cal.\ cm^3)^{0.5}\ mole^{-1}$]
$-CH_3$	31.8	218
$-CH_2-$	16.5	132
$>CH-$	1.9	23
$>C<$	−14.8	−97
$>C_6H_3-$	41.4	562
$-C_6H_4-$	58.5	652
C_6H_5-	75.5	735
$CH_2=$	29.7	203
$-CH=$	13.7	113
$>C=$	−2.4	18
$-OCO-$	19.6	298
$-CO-$	10.7	262
$-O-$	5.1	95
$-Cl$	23.9	264
$-CN$	23.6	426
$-NH_2$	18.6	275
$>NH$	8.5	143
$>N-$	-5.0	-3

[1] Painter et al. *Essentials of Polymer Science and Engineering*, (**2009**)

Cellulose-MAPP Monomer Configurations

Cellulose-MAPP



Note: MA group can react with cellulose OH groups at the 2, 3, or 6 carbon locations to create...

- Diester bond via covalent bonds
- Monoester bond with covalent and hydrogen bonds (OH group not reacted)
- **Changing the functionals groups will change the solubility parameter!**

$$\delta = \frac{\sum_i F_i}{\sum_i V_i} (cal.\ cm^{-3})^{0.5}$$

EQUATION 11-38

TABLE 11-1 GROUP CONTRIBUTIONS

GROUP	MOLAR VOLUME CONSTANT V^* ($cm^3\ mole^{-1}$)	MOLAR ATTRACTION CONSTANT F^* [$(cal.\ cm^3)^{0.5}\ mole^{-1}$]
$-CH_3$	31.8	218
$-CH_2-$	16.5	132
$>CH-$	1.9	23
$>C<$	−14.8	−97
$>C_6H_3-$	41.4	562
$-C_6H_4-$	58.5	652
C_6H_5-	75.5	735
$CH_2=$	29.7	203
$-CH=$	13.7	113
$>C=$	−2.4	18
$-OCO-$	19.6	298
$-CO-$	10.7	262
$-O-$	5.1	95
$-Cl$	23.9	264
$-CN$	23.6	426
$-NH_2$	18.6	275
$>NH$	8.5	143
$>N-$	-5.0	-3

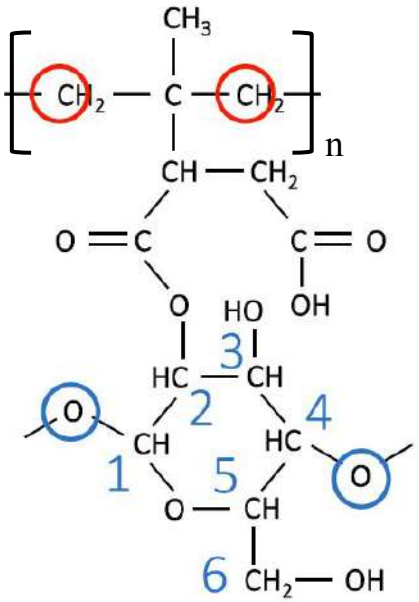
[1] Uetsuji et al. *J Mater. Sci.*, (**2020**)

[2] Painter et al. *Essentials of Polymer Science and Engineering*, (**2009**)

Cellulose-MAPP Monomer: Possibility 1

Cellulose-MAPP monomer: **C2 Model**

Possibility 1: MA group reacts with cellulose OH group at the **2 carbon** locations to create a **monoester bond**



$$\delta = \frac{\sum_i F_i}{\sum_i V_i} (cal.\ cm^{-3})^{0.5}$$

EQUATION 11-38

TABLE 11-1 GROUP CONTRIBUTIONS

GROUP	MOLAR VOLUME CONSTANT V^* ($cm^3\ mole^{-1}$)	MOLAR ATTRACTION CONSTANT F^* [$(cal.\ cm^3)^{0.5}\ mole^{-1}$]
$-CH_3$	31.8	218
$-CH_2-$	16.5	132
$>CH-$	1.9	23
$>C<$	−14.8	−97
$>C_6H_3-$	41.4	562
$-C_6H_4-$	58.5	652
C_6H_5-	75.5	735
$CH_2=$	29.7	203
$-CH=$	13.7	113
$>C=$	−2.4	18
$-OCO-$	19.6	298
$-CO-$	10.7	262
$-O-$	5.1	95
$-Cl$	23.9	264
$-CN$	23.6	426
$-NH_2$	18.6	275
$>NH$	8.5	143
$>N-$	-5.0	-3

$$\delta_{C2\ Model} = \frac{218 + 4(132) + 6(23) - 97 + 18 + 3(95) + 298}{31.8 + 4(16.5) + 6(1.9) - 14.8 - 2.4 + 3(5.1) + 19.6} = 10.94 \left(\frac{cal.}{cm^3}\right)^{0.5}$$

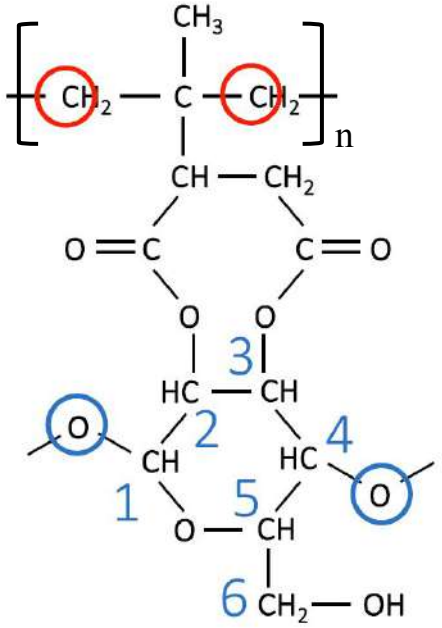
[1] Uetsuji et al. *J Mater. Sci.*, (**2020**)

[2] Painter et al. *Essentials of Polymer Science and Engineering*, (**2009**)

Cellulose-MAPP Monomer: Possibility 2

Cellulose-MAPP monomer: **C2 & C3 Model**

<u>Possibility 2</u>: MA group reacts with cellulose OH group at the **2 and 3** carbon locations to create a **diester bond**



$$\delta = \frac{\sum_i F_i}{\sum_i V_i} (cal.\ cm^{-3})^{0.5}$$

EQUATION 11-38

TABLE 11-1 GROUP CONTRIBUTIONS

GROUP	MOLAR VOLUME CONSTANT V^* ($cm^3\ mole^{-1}$)	MOLAR ATTRACTION CONSTANT F^* [$(cal.\ cm^3)^{0.5}\ mole^{-1}$]
$-CH_3$	31.8	218
$-CH_2-$	16.5	132
$>CH-$	1.9	23
$>C<$	−14.8	−97
$>C_6H_3-$	41.4	562
$-C_6H_4-$	58.5	652
C_6H_5-	75.5	735
$CH_2=$	29.7	203
$-CH=$	13.7	113
$>C=$	−2.4	18
$-OCO-$	19.6	298
$-CO-$	10.7	262
$-O-$	5.1	95
$-Cl$	23.9	264
$-CN$	23.6	426
$-NH_2$	18.6	275
$>NH$	8.5	143
$>N-$	-5.0	-3

$$\delta_{C2\&C3\ Model} = \frac{218 + 4(132) + 6(23) - 97 + 3(95) + 2(298)}{31.8 + 4(16.5) + 6(1.9) - 14.8 + 3(5.1) + 2(19.6)} = 11.20 \left(\frac{cal.}{cm^3}\right)^{0.5}$$

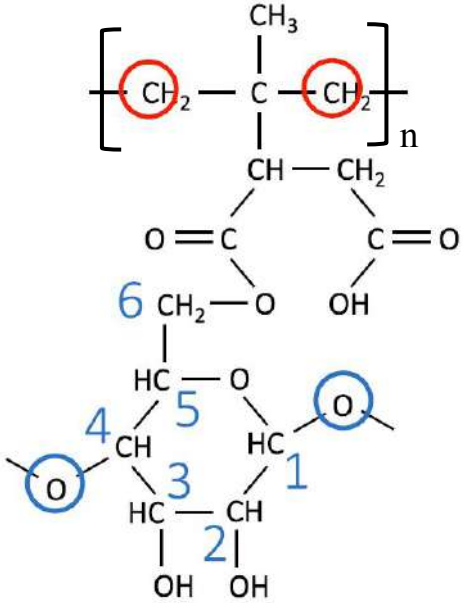
[1] Uetsuji et al. *J Mater. Sci.*, (**2020**)

[2] Painter et al. *Essentials of Polymer Science and Engineering*, (**2009**)

Cellulose-MAPP Monomer: Possibility 3

Cellulose-MAPP monomer: **C6 Model**

Possibility 3: MA group reacts with cellulose OH group at the **6 carbon** locations to create a **monoester bond**



$$\delta = \frac{\sum_i F_i}{\sum_i V_i} (cal.\ cm^{-3})^{0.5}$$

EQUATION 11-38

TABLE 11-1 GROUP CONTRIBUTIONS

GROUP	MOLAR VOLUME CONSTANT V^* ($cm^3\ mole^{-1}$)	MOLAR ATTRACTION CONSTANT F^* [$(cal.\ cm^3)^{0.5}\ mole^{-1}$]
$-CH_3$	31.8	218
$-CH_2-$	16.5	132
$>CH-$	1.9	23
$>C<$	−14.8	−97
$>C_6H_3-$	41.4	562
$-C_6H_4-$	58.5	652
C_6H_5-	75.5	735
$CH_2=$	29.7	203
$-CH=$	13.7	113
$>C=$	−2.4	18
$-OCO-$	19.6	298
$-CO-$	10.7	262
$-O-$	5.1	95
$-Cl$	23.9	264
$-CN$	23.6	426
$-NH_2$	18.6	275
$>NH$	8.5	143
$>N-$	-5.0	-3

$$\delta_{C6\ Model} = \frac{218 + 4(132) + 6(23) - 97 + 18 + 4(95) + 298}{31.8 + 4(16.5) + 6(1.9) - 14.8 - 2.4 + 4(5.1) + 19.6} = 11.23 \left(\frac{cal.}{cm^3}\right)^{0.5}$$

[1] Uetsuji et al. *J Mater. Sci.*, (**2020**)

[2] Painter et al. *Essentials of Polymer Science and Engineering*, (**2009**)

(Cellulose + MAPP) Polymer Blend Conclusion

Surface energy of pure cellulose (proportional to CED = 145.68) **decreases** when cellulose is reacted with the MA group on MAPP (average Cellulose-MAPP CED = 123.65).

- This verifies a statement given by Uetsuji *et al*.

Cellulose-MAPP Blend	**Solubility Parameter* $(Cal/cm^3)^{1/2}$**	**CED (Cal/cm^3)**
C2 Model	10.94	119.68
C2&C3 Model	11.20	125.44
C6 Model	11.23	126.11
Average	**11.12**	**123.65**

*calculated using Group Contributions Method

[1] Uetsuji et al. *J Mater. Sci.*, (**2020**)

[2] Painter et al. *Essentials of Polymer Science and Engineering*, (**2009**)

(Cellulose + MAPP) Polymer Blend Conclusion

Cellulose + MAPP polymer blend ($\Delta\delta = 2.75$) has the **smallest change in solubility parameter upon mixing** and is therefore, the **most energetically favorable** polymer blend and the **least likely to phase separate**.

$\Delta\delta\_(\text{Cellulose-MAPP}) = 2.75 \ll \Delta\delta\_(\text{MACellulose-PP}) = 4.87$

corresponding to

$\Delta G\_(\text{Cellulose-MAPP}) \ll \Delta G\_(\text{MACellulose-PP})$

Polymer Blend	**Change in Solubility Parameter* $(Cal/cm^3)^{1/2}$**
$\Delta\delta\_(\text{MACellulose-PP})$	4.87
$\Delta\delta\_(\text{Cellulose-PP})$	4.64
$\Delta\delta\_(\text{MACellulose-MAPP})$	2.98
$\Delta\delta\_(\text{Cellulose-MAPP})$	2.75

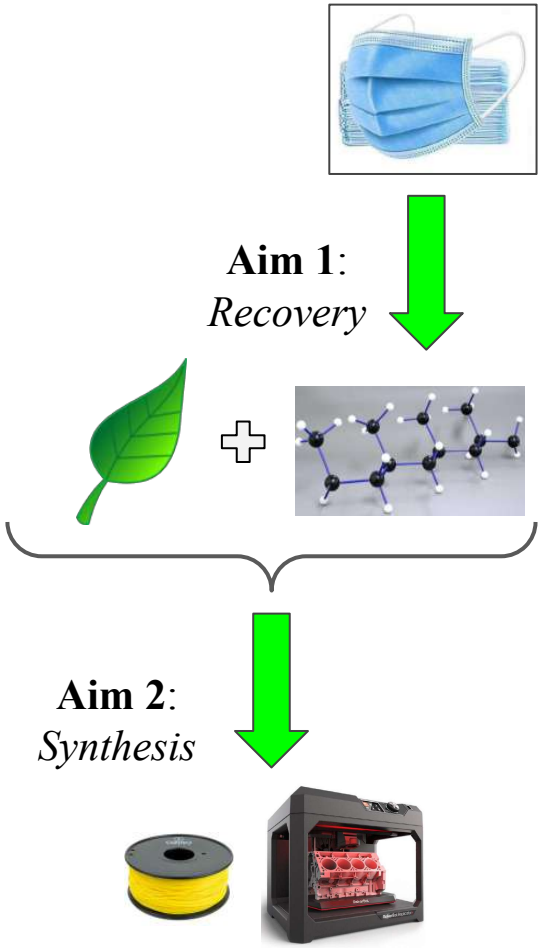
*calculated using Group Contributions Method

(Cellulose + MAPP) polymer blend is our most stable combination.

[1] Painter et al. *Essentials of Polymer Science and Engineering*, (**2009**)

Conclusion

- Motivation: Covid-19 global pandemic increased plastic pollution
  - Estimated global demand of 129 billion face masks per month [1]
  - Additive manufacturing has a need for sustainable materials
- Proposal: Recycle & recover a single-use waste (i.e., Covid-19 masks) into an extrudable paste for additive manufacturing
  - **Aim 1:** *Recover* polypropylene (PP)
    - Solvent-Targeted Recovery & Precipitation (i.e., STRAP)
  - **Aim 2:** S*ynthesize* a more sustainable extrudable polymer filament
    - Chemical surface treatment of cellulose
    - Covalently graft maleic anhydride (MA) to PP matrix
    - Create miscible cellulose-MAPP blend



Thank You!

Are there any questions?