Green composites from hop natural fiber and bioplastic

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BIOPRODUCTS DISCOVERY
& DEVELOPMENT CENTRE

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Table of contents

Properties of PBSA and PBS

Poly(butylene succinate-co-butylene adipate) (PBSA)

- Polycondensation of 1,4-butanediol, succinic acid, and adipic acid
- Copolymer
- Biodegrades faster

- Melting point: 90 – 100 °C
- Melt flow index: ≤ 10 g/10min
- Tensile strength: 25-30 MPa
- Notched impact strength: ≥ 12 kJ/m

- Aliphatic polyester
- Semi-crystalline
- Biodegradable
- Can be petroleum based or bio-based

- Elongation at break: ≥ 300%

Poly(butylene succinate) (PBS)

- Polycondensation of 1,4-butanediol and succinic acid
- Homopolymer
- Higher crystallinity
- 84 700 tonnes produced per year

- Melting point: 110 - 116 °C
- Melt flow index: ≤ 20 g/10min
- Tensile strength: 35-45 MPa
- Notched impact strength: ≥ 5 kJ/m

[1] Müller, R.-J.; Witt, U.; Rantze, E.; Deckwer, W.-D. Architecture of Biodegradable Copolyesters Containing Aromatic Constituents. *Polymer Degradation and Stability* **1998**, *59* (1), 203–208.

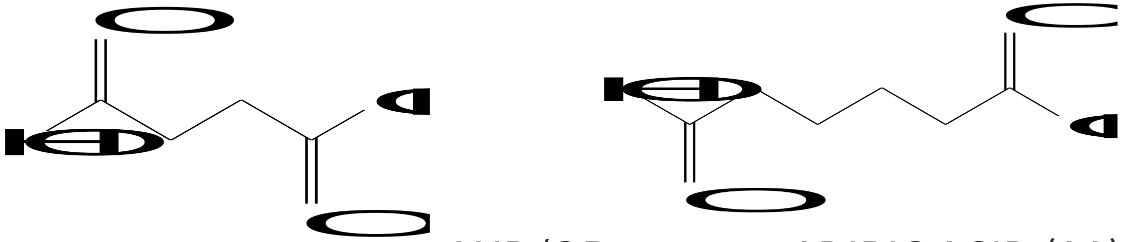
[2] Papageorgiou, G. Z.; Achilias, D. S.; Bikiaris, D. N. Crystallization Kinetics of Biodegradable Poly(Butylene Succinate) under Isothermal and Non-Isothermal Conditions. *Macromolecular Chemistry and Physics* **2007**, *208* (12), 1250-1264.

[3] Vroman, I.; Tighzert, L. Biodegradable Polymers. *Materials (Basel)* **2009**, *2* (2), 307–344.

[4] PBS Specifications. Tunhe, China.

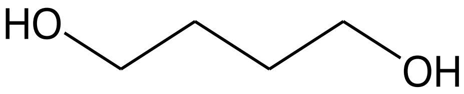
PBSA and PBS bioplastics

1,4-Butanediol (BDO) & Succinic acid (SA) and/or Adipic acid (AA) (1.1:1)

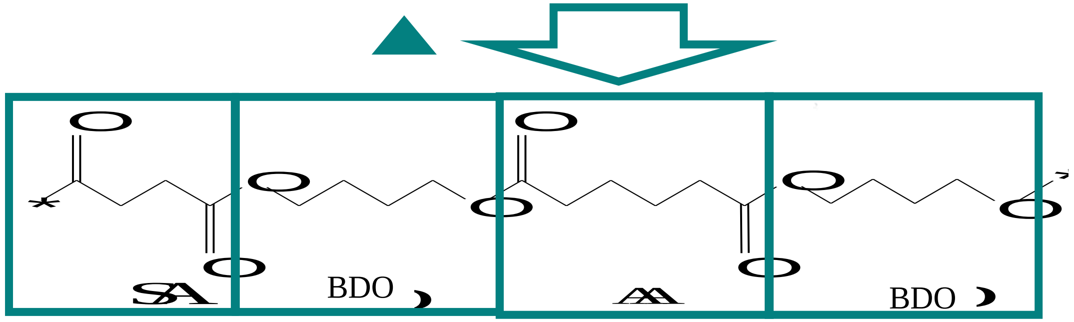


SUCCINIC ACID (SA) AND/OR ADIPIC ACID (AA)

+

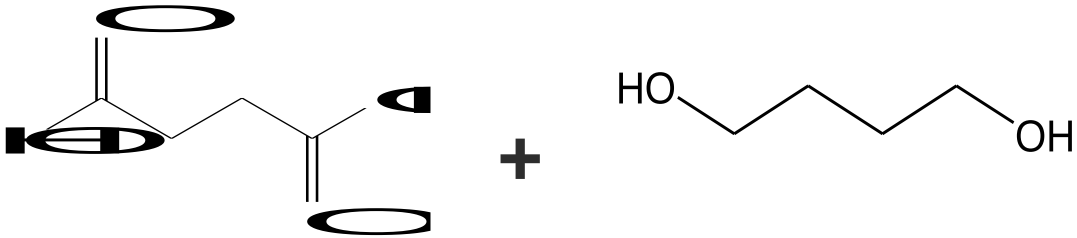


1,4-Butanediol (BDO)

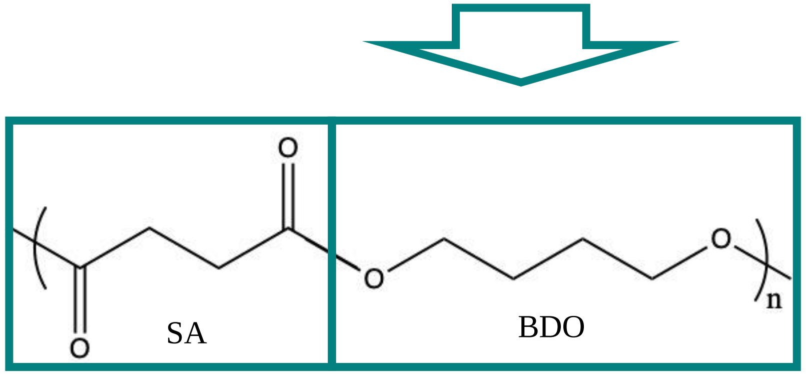


+ H_2O

PBSA- POLY(BUTYLENE SUCCINATE-CO-BUTYLENE ADIPATE)



SUCCINIC ACID (SA) 1,4-Butanediol (BDO)



+ H_2O

PBS- POLY(BUTYLENE SUCCINATE)

[1] Debuissy, T.; Pollet, E.; Avérous, L. Synthesis and Characterization of Biobased Poly(Butylene Succinate-Ran-Butylene Adipate). Analysis of the Composition-Dependent Physicochemical Properties. *European Polymer Journal* **2017**, *87*, 84–98

[2] Pérez-Camargo, R. A.; Fernández-d'Arlas, B.; Cavallo, D.; Debuissy, T.; Pollet, E.; Avérous, L.; Müller, A. J. Tailoring the Structure, Morphology, and Crystallization of Isodimorphic Poly(Butylene Succinate-Ran-Butylene Adipate) Random Copolymers by Changing Composition and Thermal History. *Macromolecules* **2017**, *50* (2), 597–608.

Biodegradable

- **The polymer will break down if exposed to microorganisms**
- Hydrolysable ester bonds and short aliphatic chains
- Diacids and diols influence the biodegradability
  - Determine the accessibility of the hydrolytic or enzymatic active site for degradation processes
- Degradation occurs at carbonyl group (C=O in the ester)

Example of a Non-Biodegradable Polyester

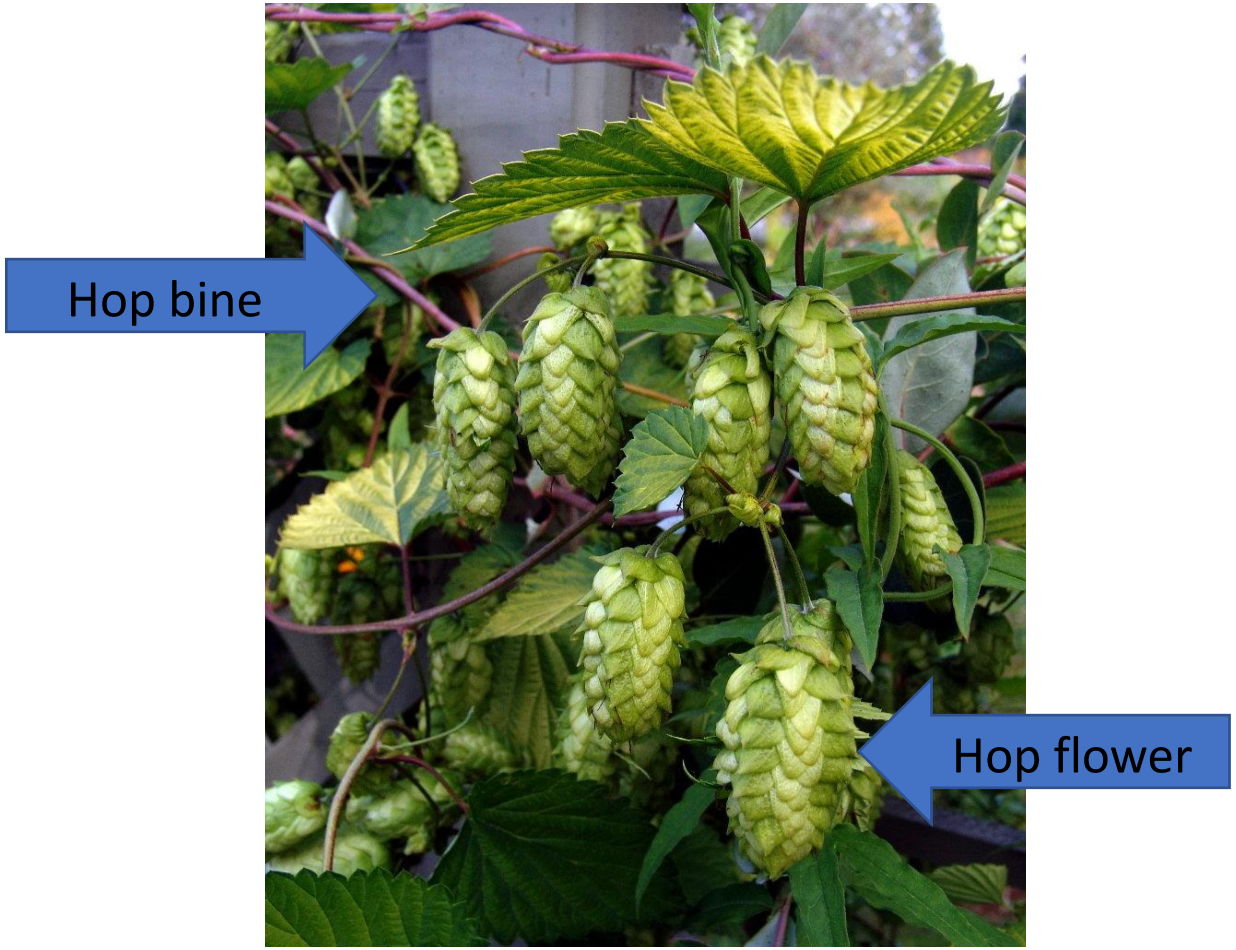
- Polycarbonate is a polyester that is non-biodegradable
  - Aromatic rings cannot undergo hydrolytic and enzymatic degradation
  - Carbonyl bond is inaccessible to enzymes because of the presence of bulky phenyl groups on either side

Bio-based

- PBSA can be petroleum-based or bio-based
- **Bio-based means derived from renewable sources**
- Advantageous for PBSA as it can have variety of applications

[1] Müller, R.-J.; Witt, U.; Rantze, E.; Deckwer, W.-D. Architecture of Biodegradable Copolyesters Containing Aromatic Constituents. *Polymer Degradation and Stability* **1998**, *59* (1), 203–208.
[2] Vroman, I.; Tighzert, L. Biodegradable Polymers. *Materials (Basel)* **2009**, *2* (2), 307–344. (1)
[3] Okada, M. Chemical Syntheses of Biodegradable Polymers. *Progress in Polymer Science* **2002**, *27* (1), 87–133.

Hop Fiber



Humulus lupulus

Mainly used in the **brewing industrial**
- Preserve and flavour beer
- Only hop flowers used

The hop bines and leaves are cut and discarded after harvesting the flowers; makes up **75% of the biomass**

United States produced **115,630,900 pounds** of hop flowers in 2021 (National Hop Report provided by USDA)

No studies have been done using hop fibers in composites with PBSA or any other polymers

[1] Reddy, N.; Yang, Y. Fibers from Hop Stems. In *Innovative Biofibers from Renewable Resources*; Reddy, N., Yang, Y., Eds.; Springer: Berlin, Heidelberg, 2015; pp 43–44.
[2] https://downloads.usda.library.cornell.edu/usda-esmis/files/s7526c41m/08613p220/05742t06k/hopsan21.pdf
[3] http://media.oregonlive.com/homesandgardens/photo/goldenhopsjpg-020a19dc7d86229a.jpg

Materials and Methods

Materials & Methods: *Fiber preparation*

Materials Advances

ROYAL SOCIETY OF CHEMISTRY

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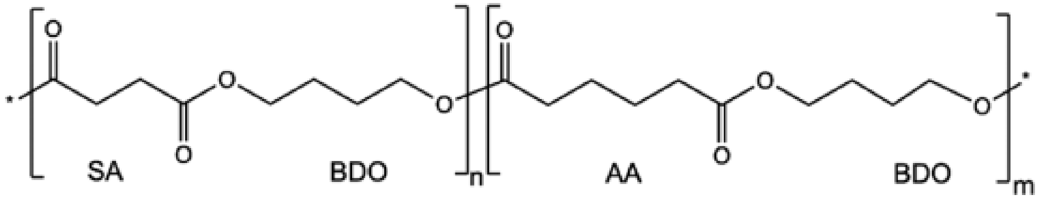
Hop natural fiber-reinforced poly(butylene succinate-*co*-butylene adipate) (PBSA) biodegradable plastics: effect of fiber length on the performance of biocomposites

Nicole Harder,[ab] Arturo Rodriguez-Uribe,[a] Michael R. Snowdon,[a] Manjusri Misra*[ab] and Amar K. Mohanty[ab]

POLYMER PBSA



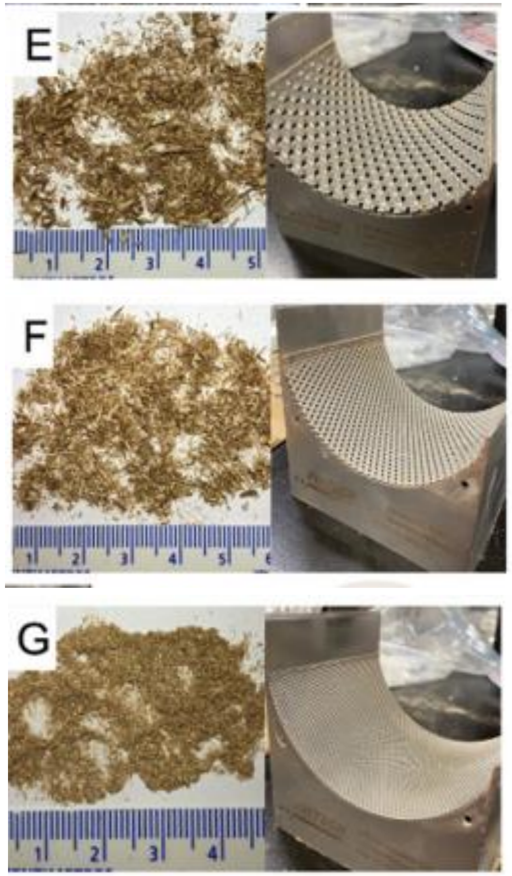
A=Hop bines

B, C & D= Size reduction

E=0.25 mm FIBER

E=1.0 mm FIBER

E=2.0 mm FIBER



Materials & Methods: *DSM Processing; Extrusion-Injection-compatibilization and molding*

30wt.%Fiber

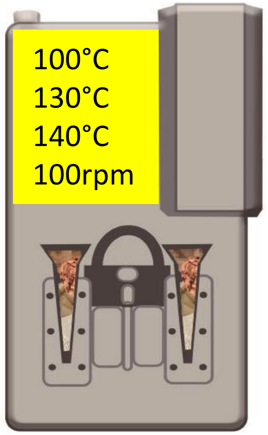
Less than 0.25 mm fiber

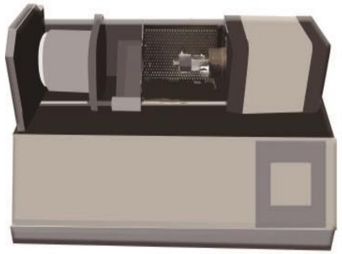
Less than 1 mm fiber

Less than 2 mm fiber

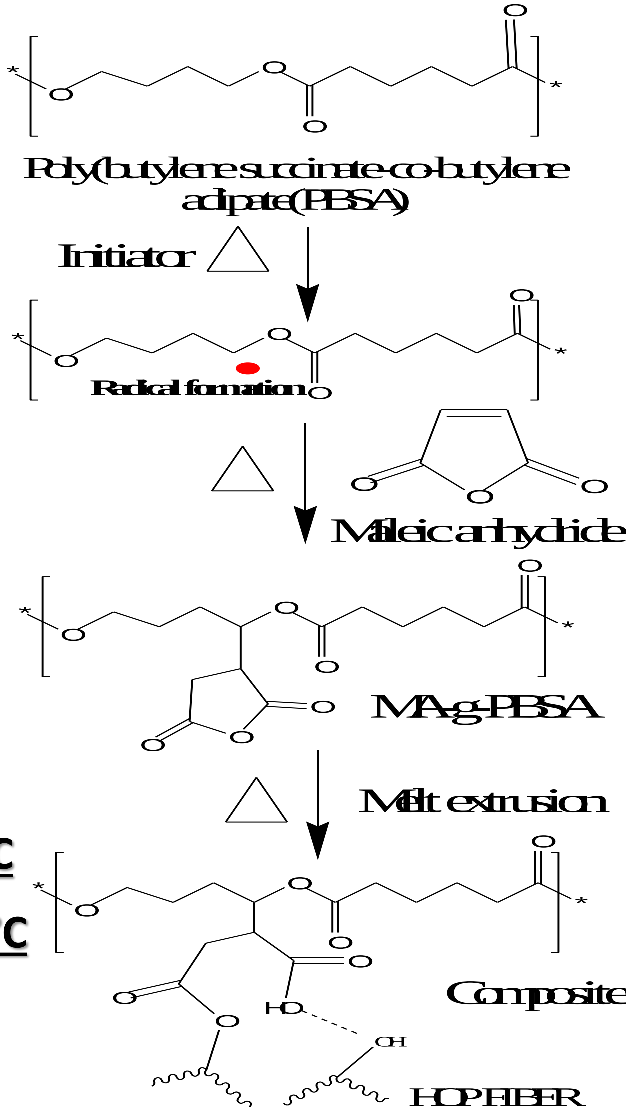
%PBSA

%MA-g-PBSA





- **Mold temperature of 30°C**
- **Melt temperature of 140°C**
- **Pressure and timing: 10 bars and 21 seconds, respectively.**

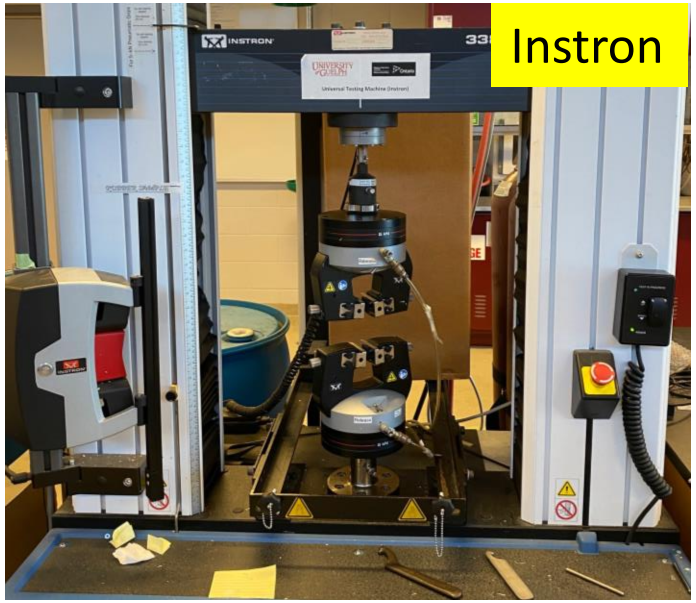


COMPOSITES

PBSA

PBSA/Hop 1mm

Materials & Methods: *Mechanical Characterization*



Tensile properties

Flexural properties

Impact properties

Materials & Methods: *Rheological Characterization*

Anton Paar Rheometer

- Complex Viscosity
- Storage modulus
- Loss modulus

Melt flow index (MFI)

- Resistance of the flow of melt

Materials & Methods: *Chemical and Morphological Characterization*

Fourier-transform infrared spectroscopy (FTIR)

- Spectrum
- Functional groups of material

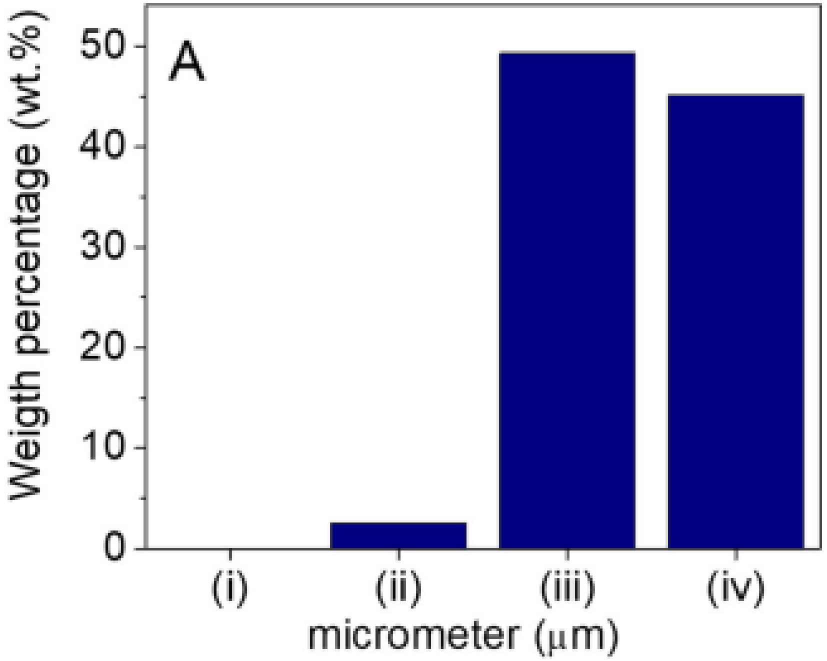
Scanning electron microscope (SEM)

- Microscope
- Morphology

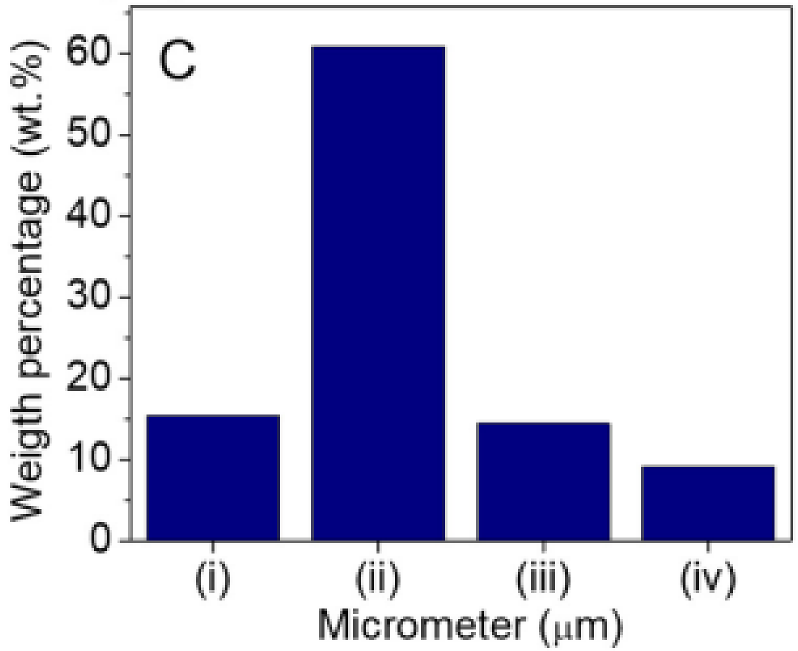
Results

FIBER SIZE DISTRIBUTION

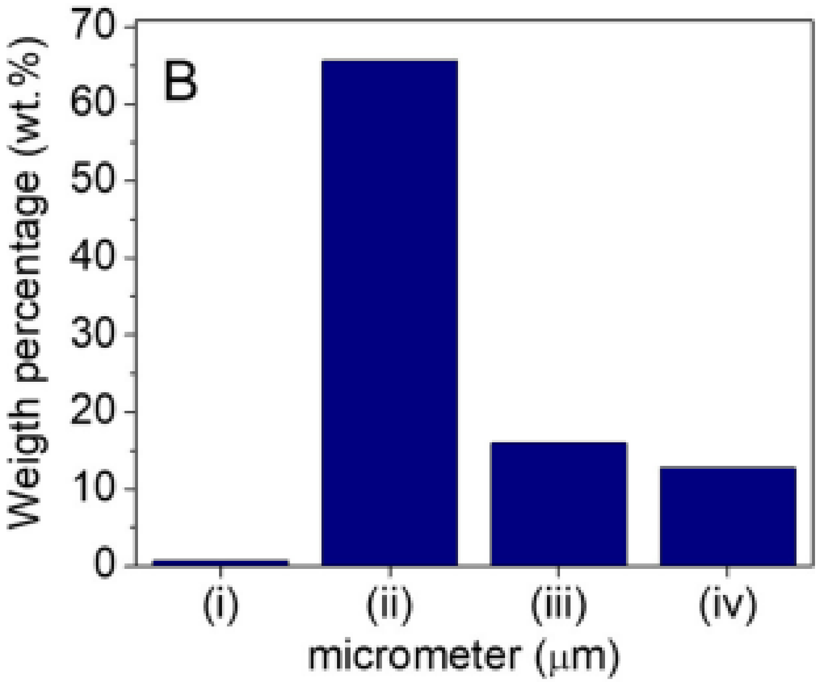
A= 0.25 mm



A= 1.0mm

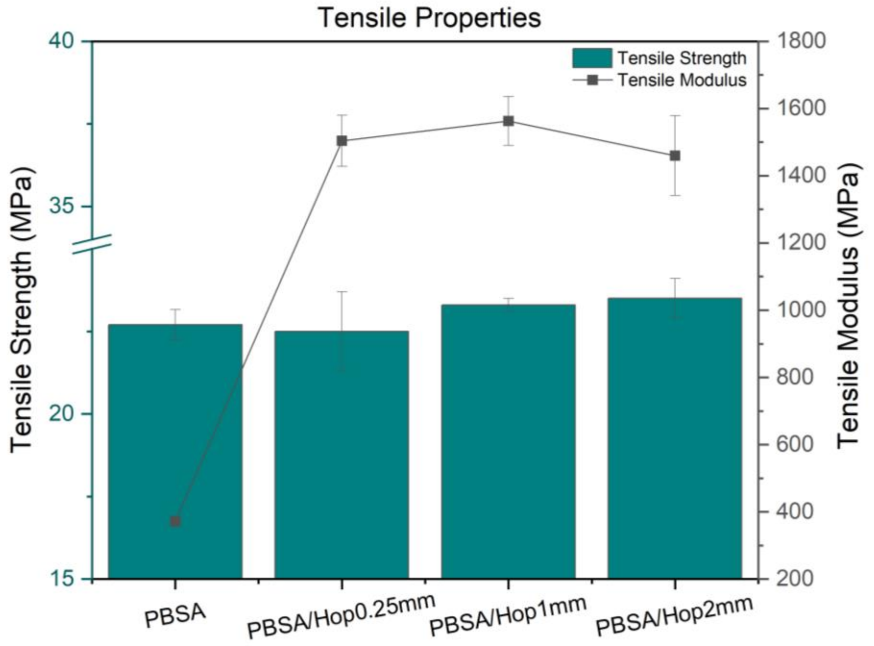


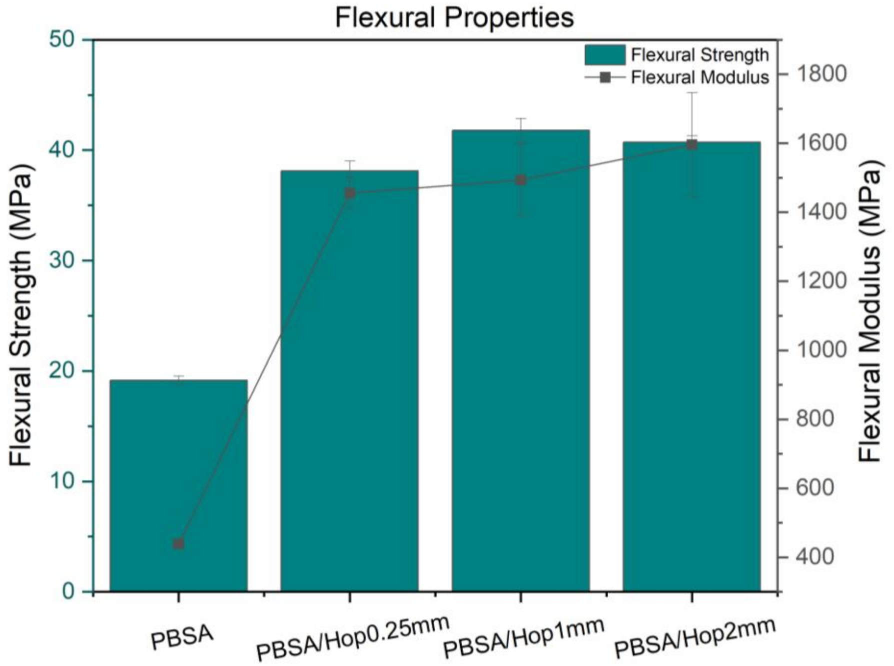
A= 2.0 mm



Larger than 1000 (i), 1000 4 x 4 300 (ii), 300 4 x 4 150 (iii), and smaller than 150 (iv) micrometers

- **It was found that 1mm fiber has less particle dispersion.**



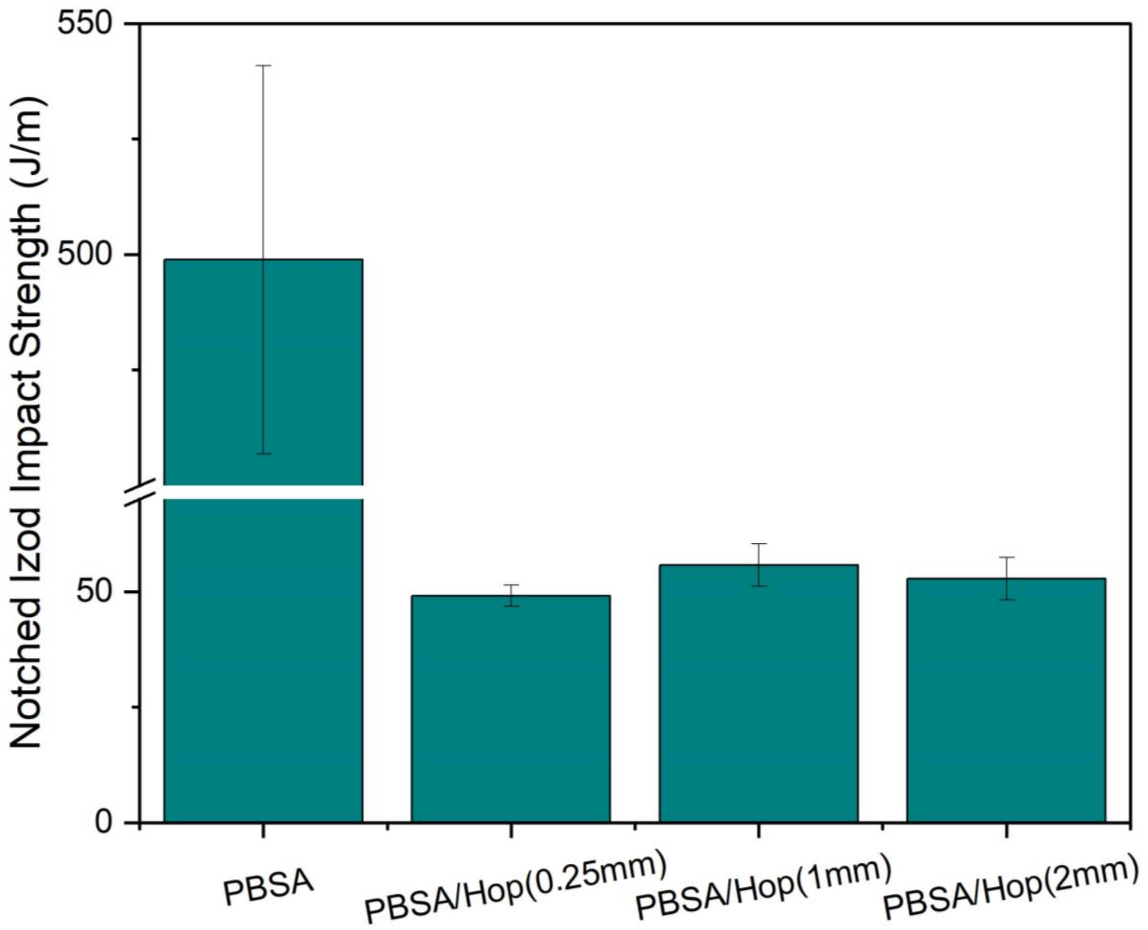


Tensile and Flexural Properties

- Overall, best performance in 1 mm fiber-based composites

	Elongation at yield (%)	Elongation at break (%)
Neat PBSA	15.53 ± 0.2	525.89 ± 19
PBSA/Hop (0.25 mm)	4.34 ± 0.3	4.47 ± 2.8
PBSA/Hop (1 mm)	4.10 ± 0.2	5.46 ± 0.5
PBSA/Hop (2 mm)	4.17 ± 0.4	5.07 ± 1.1
Coupled composites	5.6±0.4	5.9±0.4

Impact Properties

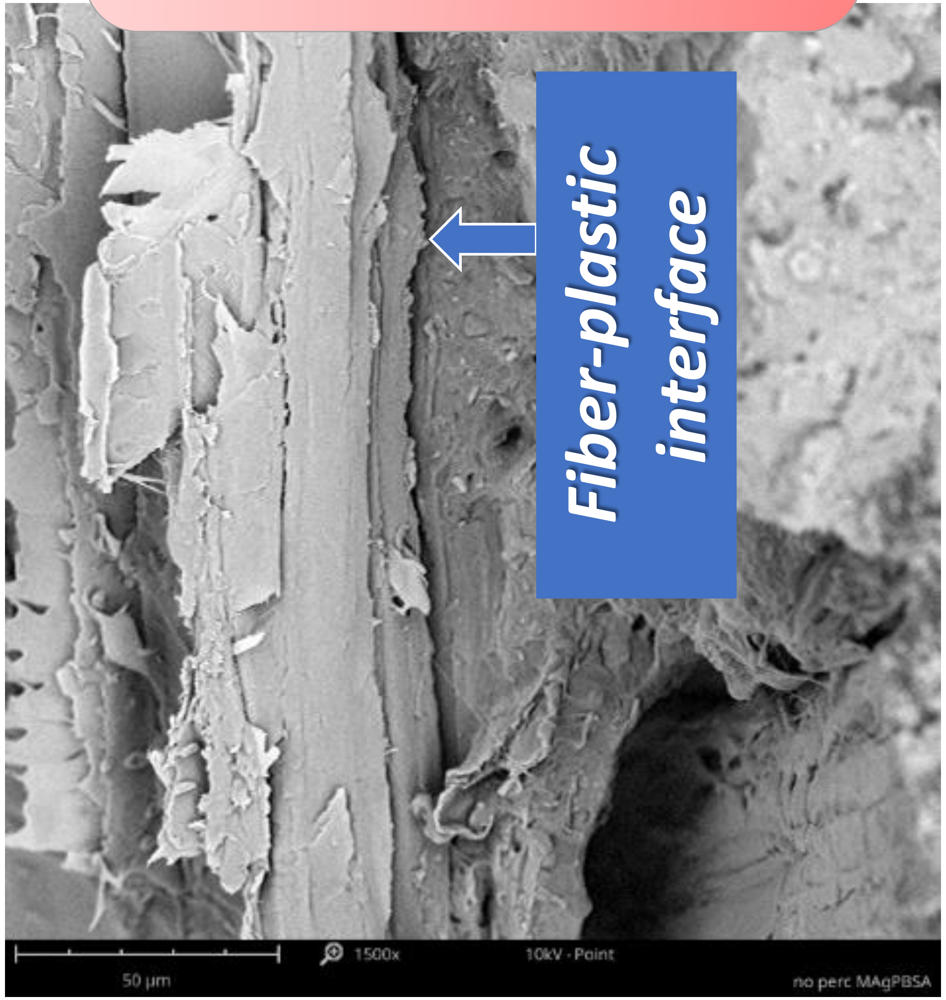


2.75 J pendulum

Neat PBSA	**498 ± 42 J/m**
PBSA/Hop (0.25 mm)	**49 ± 2.3 J/m**
PBSA/Hop (1 mm)	**55 ± 4.6 J/m**
PBSA/Hop (2 mm)	**52 ± 4.6 J/m**
Coupled composites	**66±3 J/m**

- 1 mm had the higher strength, shows better performance.
- Compatibilized composites with MA-g-PBSA showed improved performance.

Uncompatibilized composites



Compatibilized composites

Conclusions

- The addition of the coupling agent (MA-g-PBSA) improves the interfacial adhesion between the plastic matrix and the natural fiber
- As a result, the tensile strength of compatibilized composite was similar as compared to neat PBS.
- The tensile strength of compatibilized composites increase in 50% respect to non-compatibilized composites
- The overall properties of the compatibilized composites was superior as compared to those not compatibilized.
- The inclusion of the fiber increased the HDT from ~60C to 90C