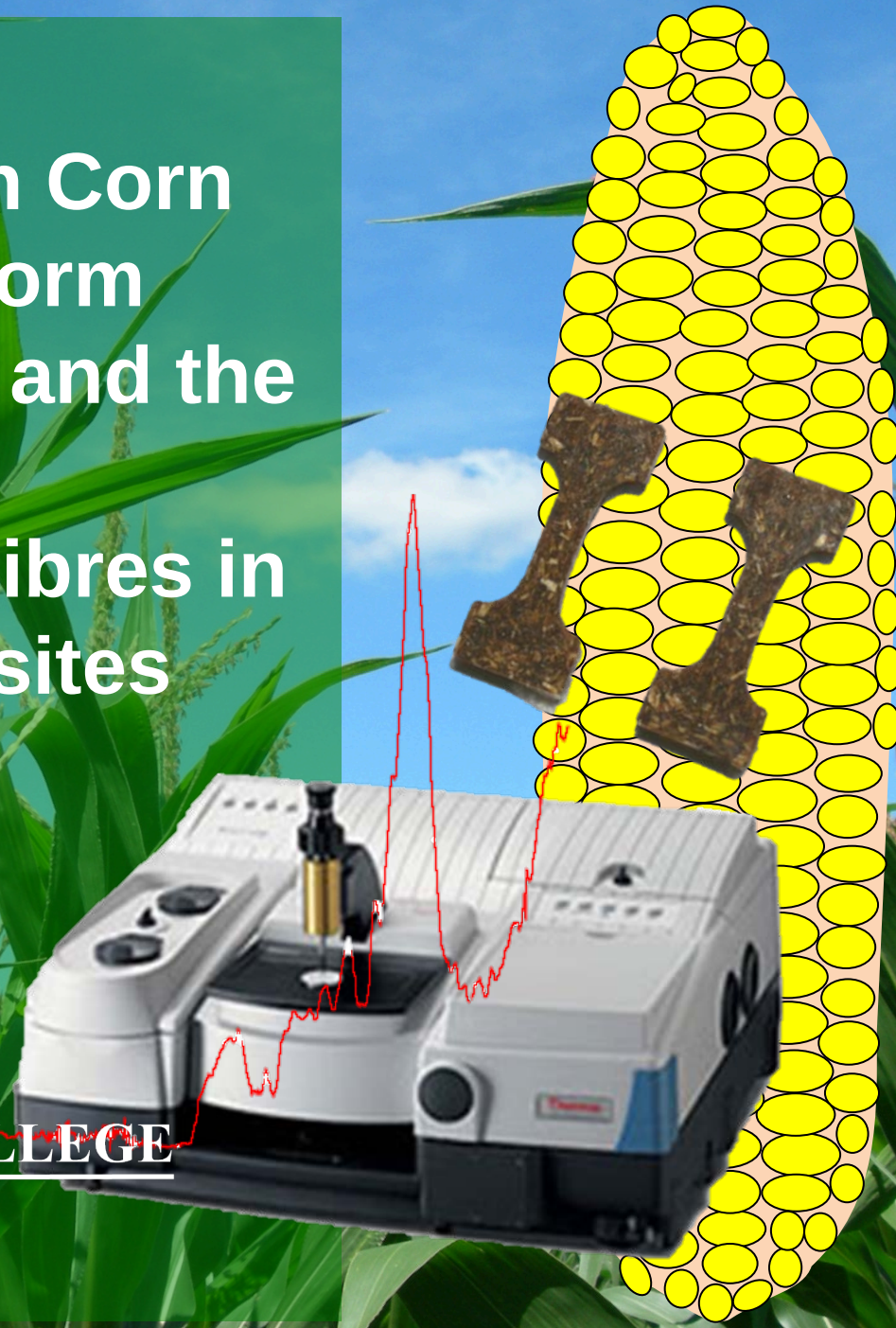
Measurement of Fibre Compositional Traits in Corn Stalk by Fourier-transform Infrared Spectroscopy and the Thermal Stability of Processed Corn Cob Fibres in Polypropylene Composites

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UNIVERSITY of GUELPH

ONTARIO AGRICULTURAL COLLEGE

DEPARTMENT OF PLANT AGRICULTURE

PEOPLE:

- **Postdoc:**
  - **Muhammad Arif**
- **Masters student: Muhammad Riaz**



Muhammad Riaz



Dr. Muhammad Arif

OVERALL GOAL:

- **Improve plant biomass fibres for use in biocomposite manufacture**







Plant Biomass for the Bioeconomy:

- **Can be derived from:**
  - **dedicated biomass crops such as Miscanthus and switchgrass, or**
  - **residue from food crops**
- **We have explored the potential of breeding food crops for multiple purposes**
  - **food and biocomposite production**





SOY, CORN, AND WHEAT BIOMASS IN ONTARIO

- **2016 production**
  - ➢**1.09 million ha of soybean**
  - ➢**0.81 million ha of corn**
  - ➢**0.44 million ha of wheat**



Stem biomass available from major Ontario crops:

Crop	Stem material (t/ha)	Recoverable stem biomass (t/ha)	Total recoverable stem biomass (million t)
Corn	**7.4**	**5.2**	**3.3**
Soy	**2.5**	**2.2**	**1.8**
Wheat	**8.0**	**6.0**	**2.9**

Ontario Agriculture Census, 2006, Stat. 2010

PLANT FIBERS IN COMPOSITE MANUFACTURE

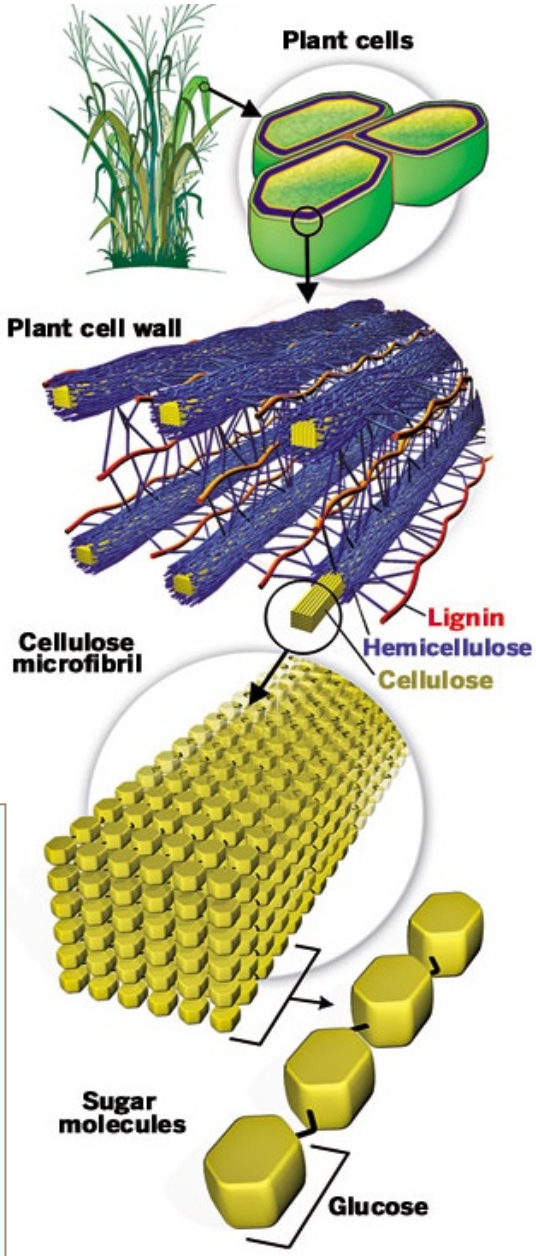
- **Plant fibers can be used in the manufacture of automobile parts as replacements for glass fibers in composites with plant- or petroleum-based plastics**

- **Advantages**:
  - **lower material costs than plastic matrices and glass fibres (plant fibre $ 0.8/kg; glass fibre $ 2/kg)**
  - **lighter materials – reduced fuel consumption**
  - **bio-based materials are C-neutral**
  - **biodegradable**



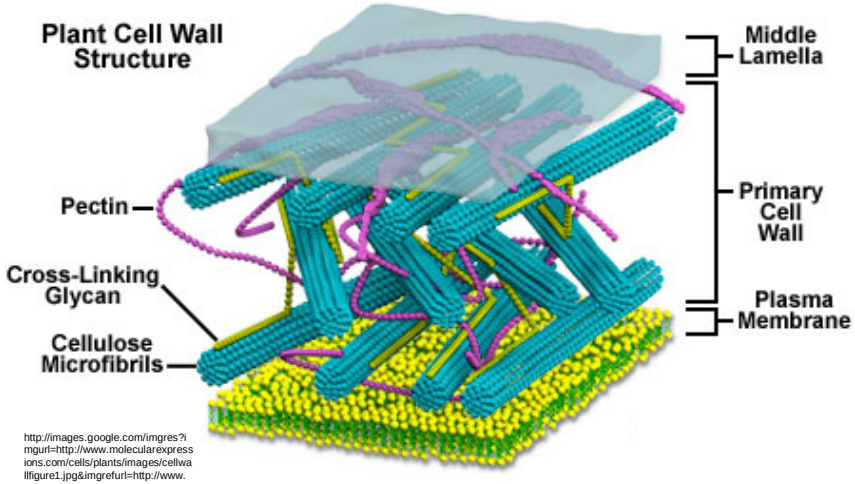
Mohanty et al



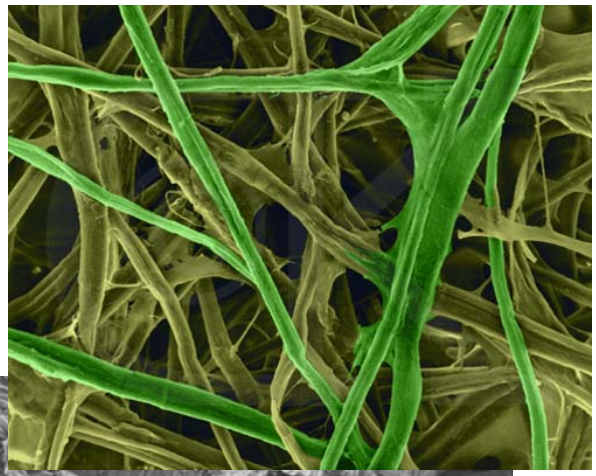


CAUSES OF LOW PLANT FIBRE/ COMPOSITE PERFORMANCE:

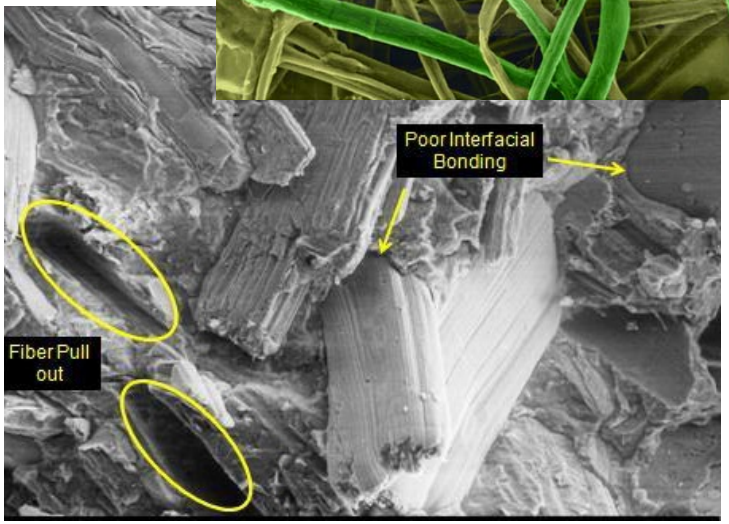
- natural fibre composed of cellulose monofilaments associated with hemi-cellulose, which is connected with lignin
- thermal degradation of fibre components caused by the relatively high temperatures (~ 200 ^{o}C) necessary to melt resins
- lack of molecular interaction between the natural fibres and plastic resins



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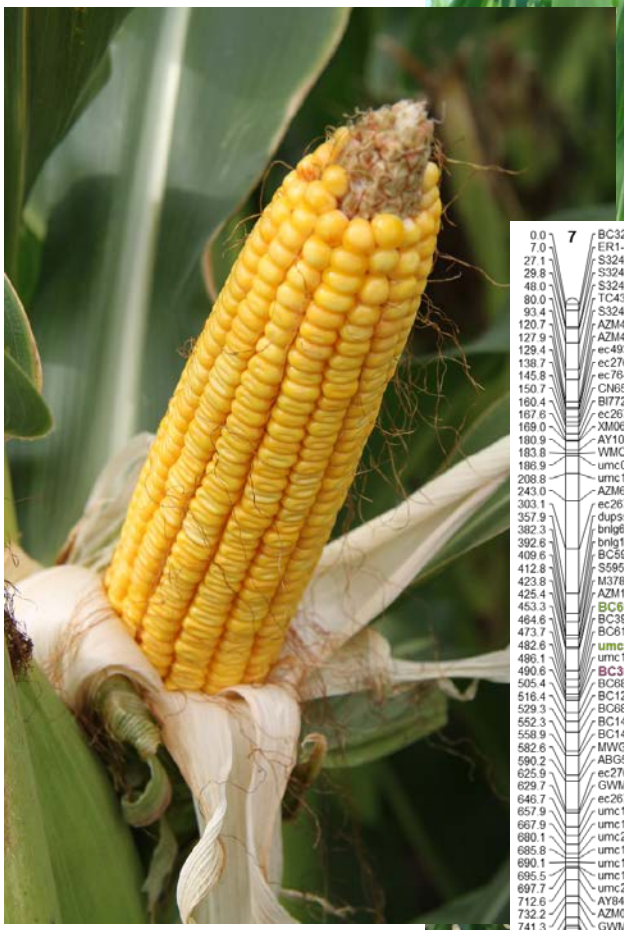


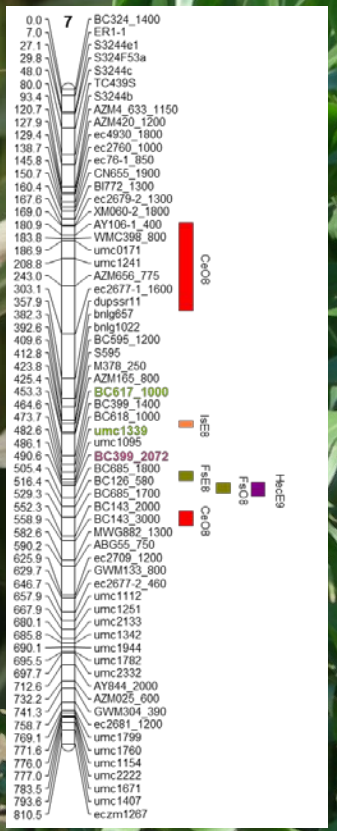
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OVERALL OBJECTIVES:

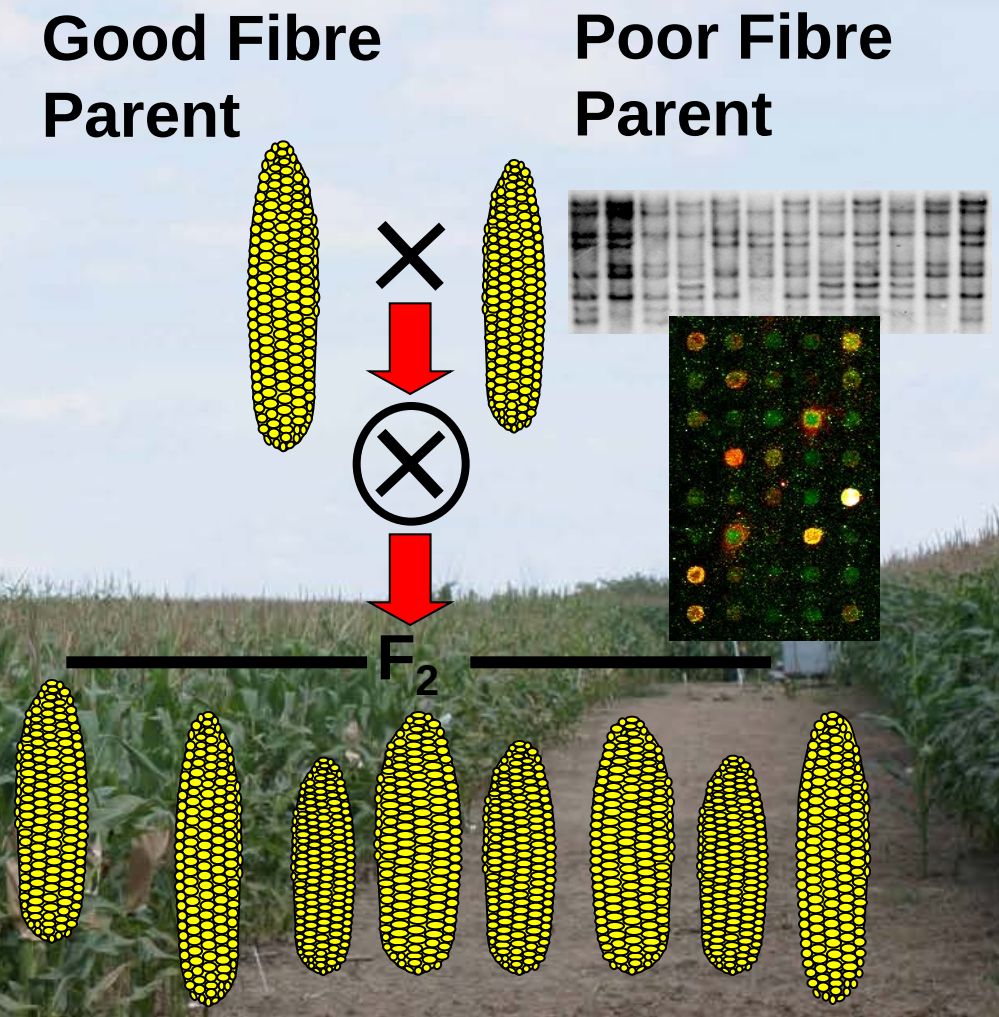
- Understand the genetic basis for corn fibre performance in biocomposites
- Develop methods for selecting corn genotypes with superior fibres for biocomposite manufacture





PREVIOUS WORK:

- screened corn breeding lines for variation in fibre composition and composite performance
- crossed a low performer with a high performer to create a segregating population
- characterized individuals in the population for:
  - fibre composition;
  - fibre performance characteristics; and
  - genetic makeup
- identified correlations among:
  - fibre composition
  - fibre performance; and
  - genetic makeup



CORRELATIONS AMONG CORN FIBER AND COMPOSITE (POLYPROPYLENE) TRAITS

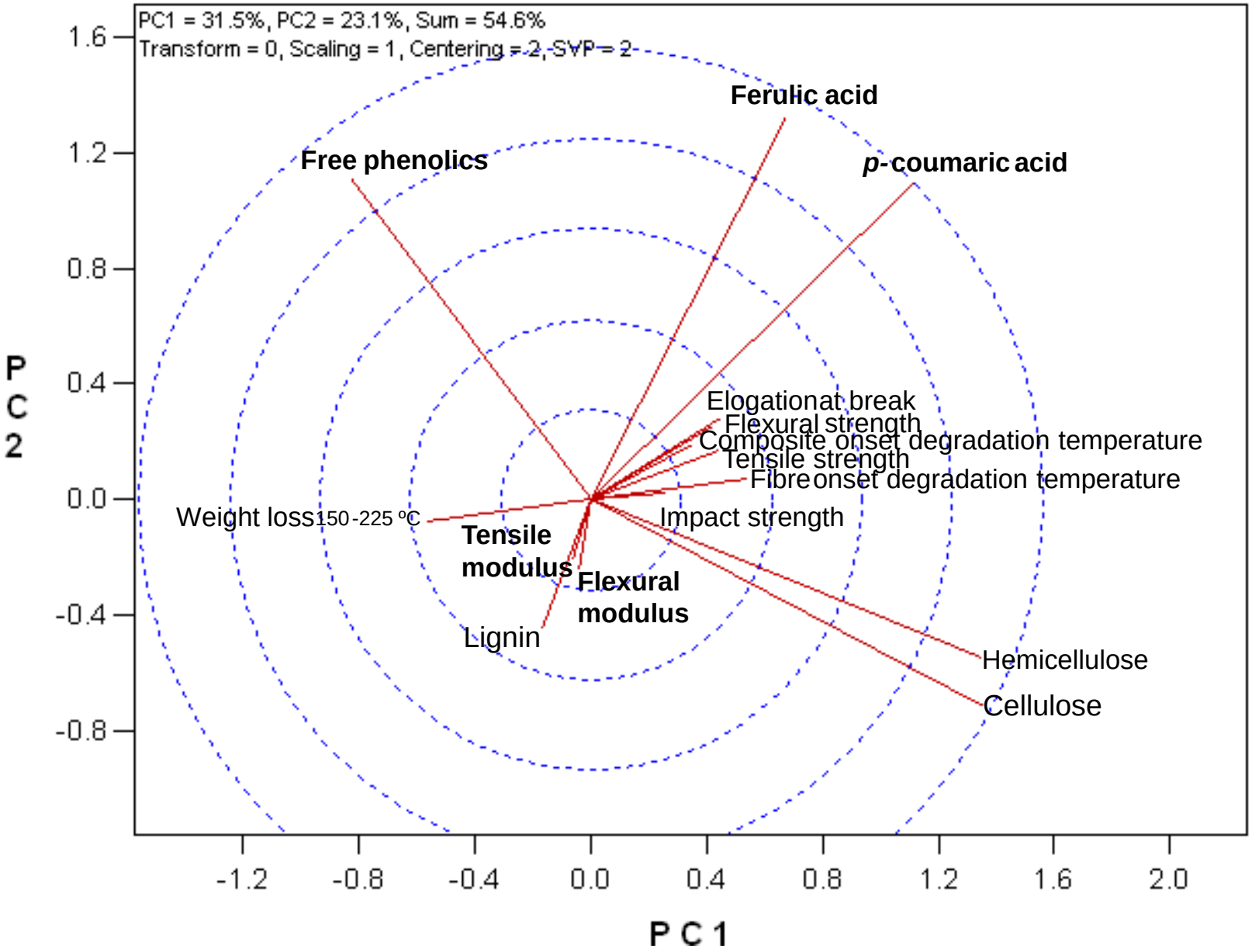
Correlation between:

- Fiber traits
- Composite traits
- Selection trait (seed ferulic acid content) & …
- Fibers & Composites

	FIBERS						COMPOSITE					SELECT.
Trait	**Neutral detergent fiber (NDF)**	**Acid detergent fiber (ADF)**	**Hemicellulose (HC)**	**Cellulose, Elora [C(E)]**	**Cellulose, Ottawa [C(O)]**	***p*-coumaric acid (PC)**	**Impact strength (IMP)**	**Tensile strength (TS)**	**Tensile modulus (TM)**	**Elongation at break point (EBP)**	**Flexural strength (FS)**	**Ferulic acid, seed (EFA**
Acid detergent fiber (ADF)	0.95**											
Hemicellulose (HC)	0.85**	0.65**										
Cellulose, Elora [C(E)]	0.73**	0.78**	0.48**									
Cellulose, Ottawa [C(O)]	0.85**	0.85**	0.66**	0.44**								
Free phenolics (FPH)	-0.65**	-0.66**	-0.48**	-0.50**	-0.52**							
Onset degradation t, fiber (ODF)	0.92**	0.81**	0.90**	0.78**	0.80**	0.79**						
Tensile strength (TS)							0.69*					
Flexural strength (FS)								0.76*				
Flexural modulus (FM)									0.83**			
Onset degradation t, comp. (ODC)			0.65*									
Ferulic acid, seed (EFA)										-0.62*		
Diferulic acid, seed (DFA)											-0.64*	0.57**

Phenolic composition (Ferulic acid and diferulic acid negatively correlated with composite physical traits elongation (E) and flexural strength at break point (FS)

PRINCIAL COMPONENT ANALYSIS OF THE PHYSICO-CHEMICAL VARIABLES OF CORN STALK FIBRES AND PLA COMPOSITE MATERIALS



PROJECT FOCUS:

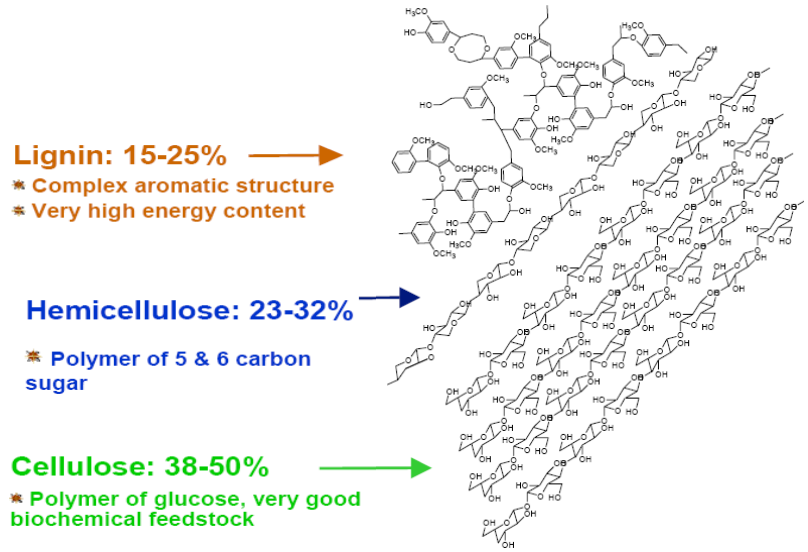
- **Test effectiveness of FT-IR to characterize corn fibre composition**
- **Test effects of fibre treatments to remove phenolics on corn cob fibre performance in biocomposites**





FIBRE ANALYSES

- Grind and sieve mature plant stems and cobs from RILs
- Characterize composition of fibre samples:
  - Free phenolics – Solvent extraction/ microplate reader
  - Cellular-bound phenolics - High Performance Liquid Chromatography (HPLC)
  - Sequential analysis of NDF, ADF and ADL (cellulose, hemicellulose, lignin) with Ankom fiber analyzer
  - Cell wall content and composition - Fourier transform infrared spectroscopy (FT-IR)









HPLC



A200 Ankom fiber analyzer



Nicolet 6700 FTIR ectrometer

DEVELOPING A STANDARD CURVE FOR FT-IR ANALYSIS OF CORN FIBRES

- Dried fibres from 2008 were analyzed using wet chemistry including:
  - ANKOM technology for cellulose, hemicellulose and lignin contents
  - HPLC was used for *p*-coumeric acid and ferulic acid for 2008 and 2009 crops
- A standard curve was developed on a limited number of fibre samples (stalk) from corn RILs to test its suitability for quantification of cellulose, hemicellulose and lignin in corn fibres
- FT-IR was used to predict cellulose, hemi-cellulose and lignin contents in the fibres of 2009 crops in Elora and Ottawa





ADVANTAGES OF FT-IR

- greater sample throughput
- non-destructive
- self calibrating
- precise measurements
- adjustable scan speed and sensitivity
- mathematically simple



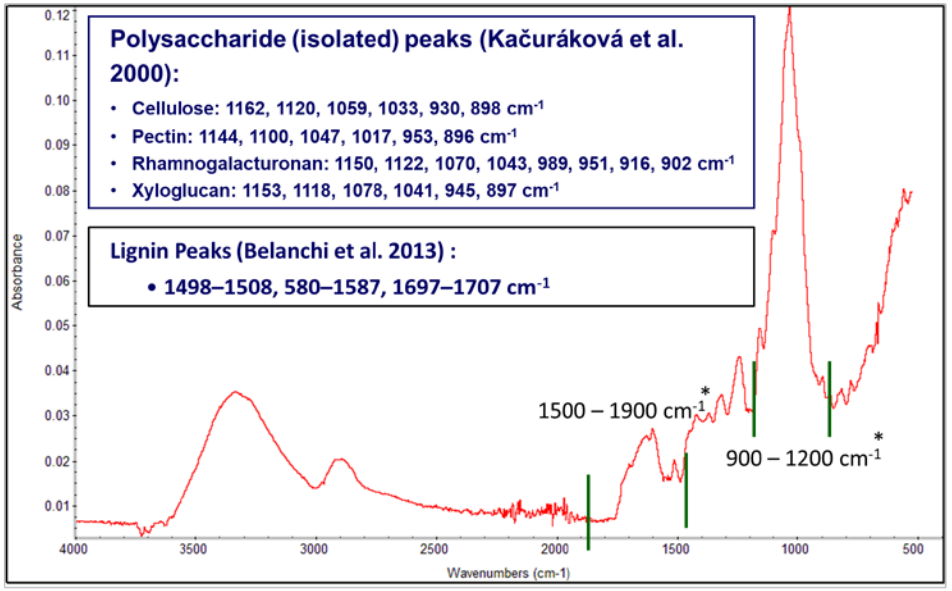


Nicolet 6700

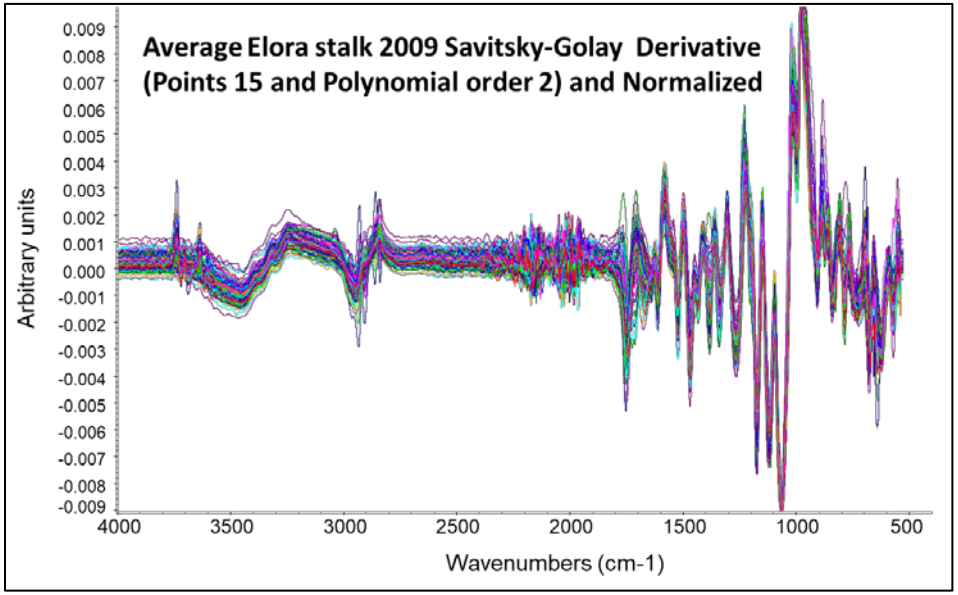
PROCEDURE (FT-IR)

- Corn stalk fibre (ground with a 2 mm screen)
- Fibre scanned from 500 to 4000 cm^{-1} in FT-IR (64 scans, resolution 4 cm^{-1})
- Samples were analyzed in duplicate
- Averaged spectra were derivatized (first Savitsky-Golay derivative; 15 units of filter width and polynomial order 2) and normalized
- Partial least square (PLS) regression was used to model the chemically analyzed stalk fibre for Cellulose, Hemicellulose and Lignin contents (regions of plant cell wall components 900-1200, 1500-1900 cm^{-1})

CORN STALK ABSORPTION SPECTRUM

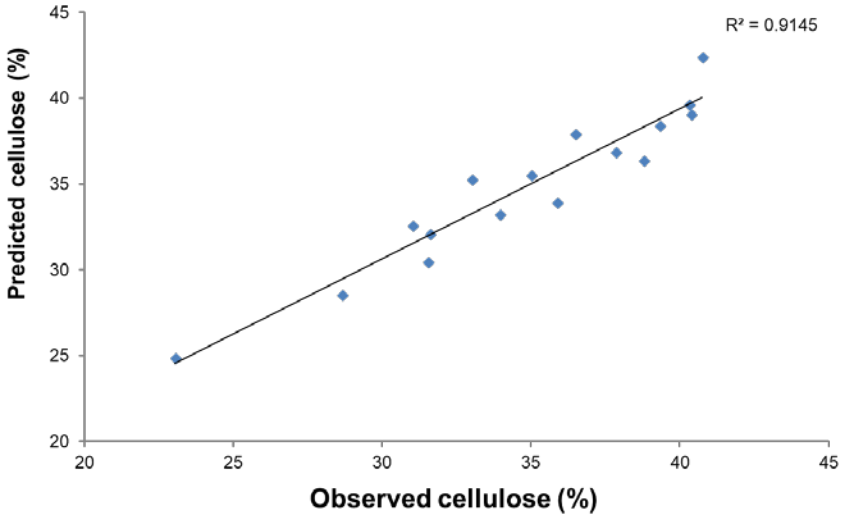


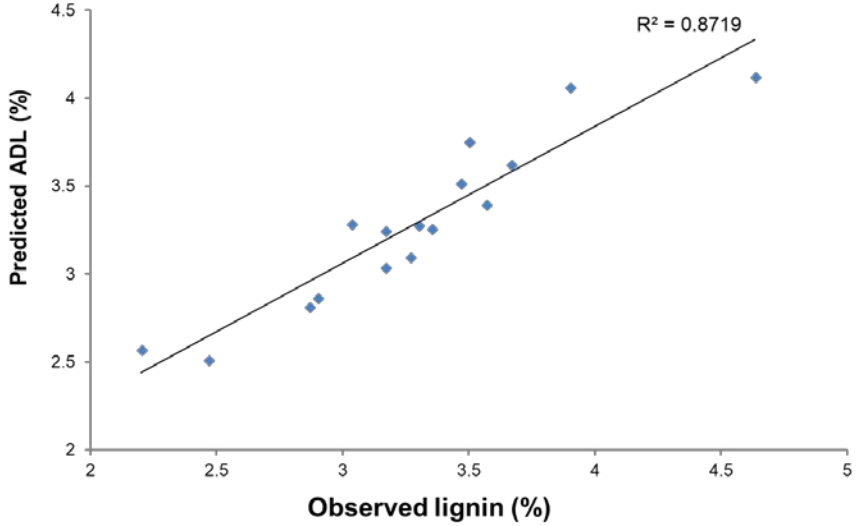
*Belanchi, A., Weisberg, M. R., Allison, G. G., Newbold, C. J. and Moorby, J. M (2013) Measurement of rumen dry matter and neutral detergent fibre degradability of feeds by Four-transform infrared spectroscopy. J. Dairy Sci. 97:2361-2375

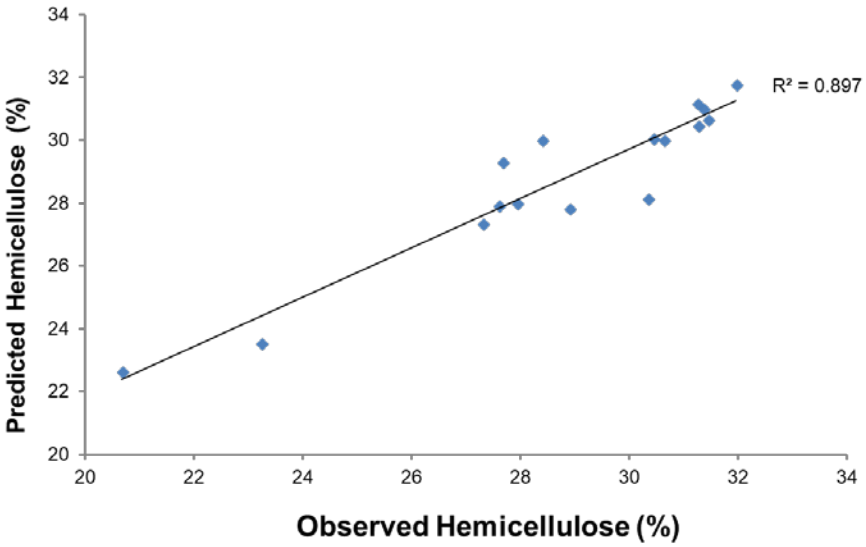


FT-IR VALIDATION

- **Observed vs predicted values determined for corn stalk fibre samples from different Recombinant Inbred Lines (RILs) grown in 2009 (sampled 3 times)**





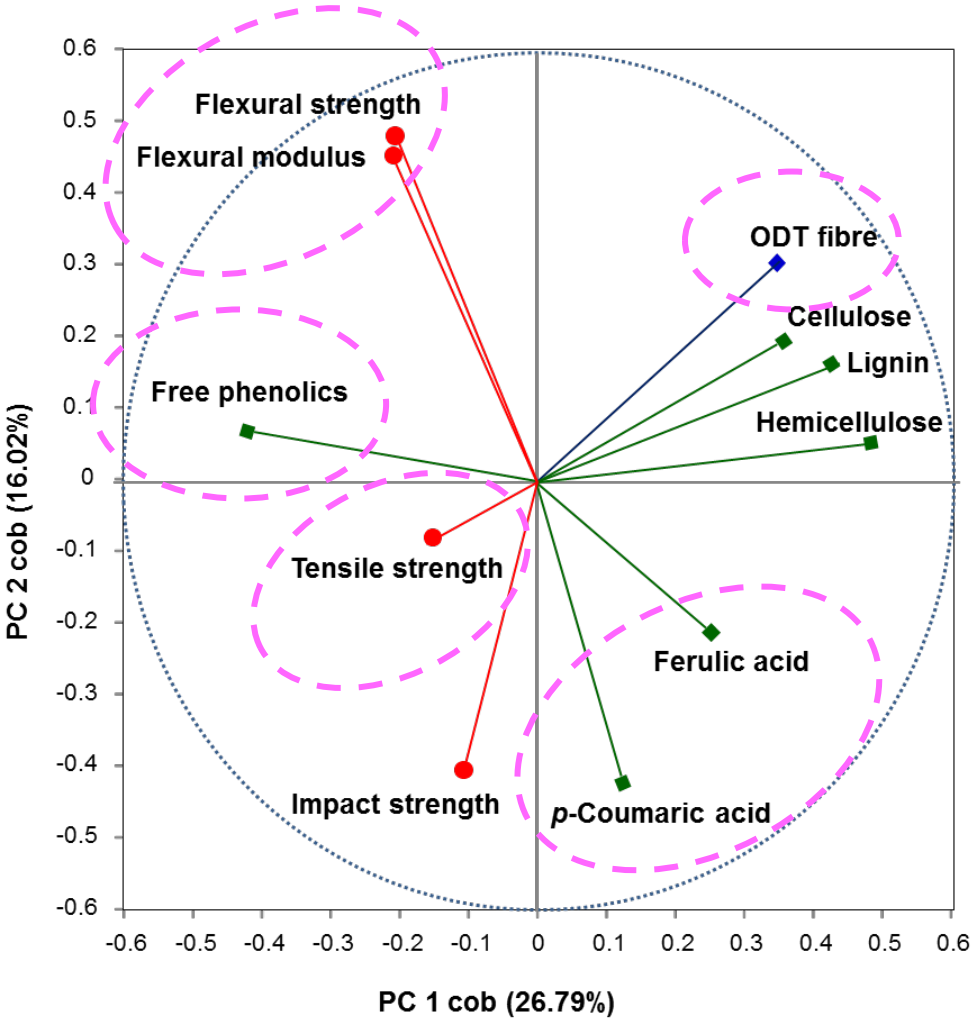


Spearman correlations between chemically analysed cell wall traits and FT-IR determined values for corn stalk fibre (*n=3*)

	Predicted Cellulose	Predicted Hemicellulose	Predicted Lignin
Wet Chemistry Cellulose	0.9618**		
Wet Chemistry Hemicellulose		0.9265**	
Wet Chemistry Lignin			0.9301**

FIBRE TREATMENT TO CONFIRM EFFECT OF CORN COB FIBRE CHEMICAL COMPOSITION ON COMPOSITE

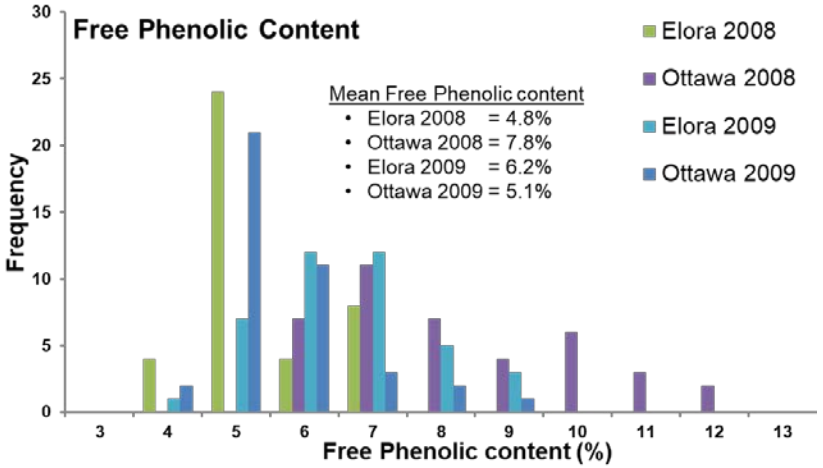
- Previous study with a polypropylene plus 20% corn cob fibre biocomposite found that:
  - Ferulic acid and p-Coumeric acid negatively correlated with Flexural strength and Flexural modulus
  - Ferulic acid and p-Coumeric acid positively related with tensile strength
  - Free phenolic levels associated negatively with onset degradation temperature of the fibre



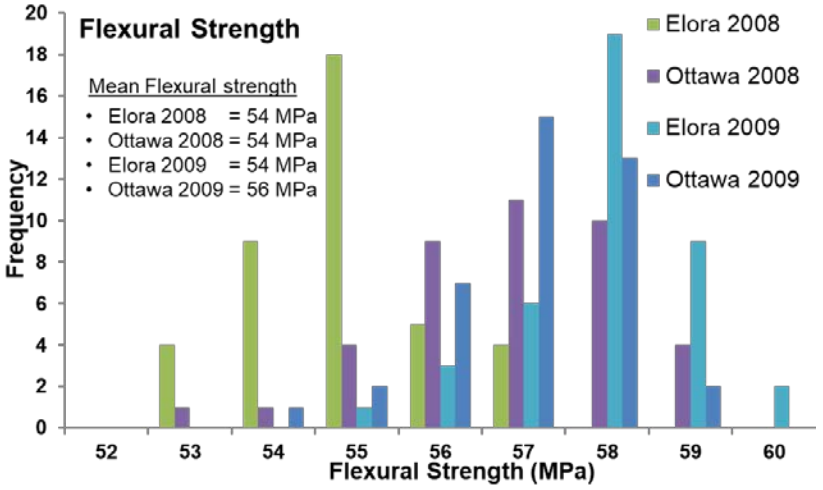
FIBRE TREATMENT TO CONFIRM EFFECT OF CORN COB FIBRE CHEMICAL COMPOSITION ON COMPOSITE

- **Hypothesis:**
  - Removal of phenolics (free phenolics, Ferulic acid and p-Coumeric) will modify behavior of corn fibre properties in composite matrices
- **Applications:**
  - Verifies rationale of selecting variety/ breeding lines with different compositions to produce composites with different properties
  - Provides a simple method for modifying fibre properties, post-isolation

Corn stalk fibre compositions - from RILs



Polypropylene corn stalk fibre composites from RILs



FIBRE TREATMENT TO CONFIRM EFFECT OF CORN COB FIBRE CHEMICAL COMPOSITION ON COMPOSITE PROPERTIES

Fibre treatment

- Corn cob fibre (RIL66 grown in Ottawa in 2009)
- Fibre processing:
  - Cutter mill, sieve size 2 mm
- Free phenolics (FP) removal:
  - Fibre treated with 50% ethanol twice almost to boil (2 repeats)
- p-Coumeric acid and Ferulic acid removal:
  - Treated with 1M NaOH @30 mg fibre with 2.5 mL 1M NaOH Shaken for 24 h at 500 rpm
- Residues dried in the fume hood

Fibre morphology



Untreated raw fibre



Free phenolics extracted



p-Coumeric acid and ferulic acid extracted

FORMULATION AND PREPARATION COMPOSITES

Formulation

- Corn cob fibre (RIL66 Grown in Ottawa in 2009)
- Processed with a Cutter mill, sieved size 2 mm
- Corn cob fibre treatments:
  - Untreated (Natural fibre)
  - Free phenolics removed
  - p-Coumeric and ferulic acid removed
- Fibre content in the composites = 30% (wt/wt)
- PP (1112Z; Pinnacle Polymers) MFI: 12g/10minutes) 68%
- Coupling agent:
  - 2 % (ARKEMA grafted Maleic anhydride polypropylene OREVAC® CA-100)



Processing

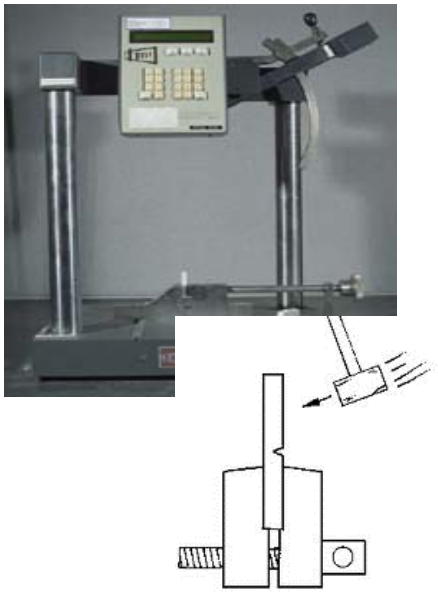
- Extrusion (DSM extruder): twin screw, 190°C, 40 rpm, 1 min
- Injection molding conditions: 190°C barrel, 50°C mold temperature, 8 bars pressure, 8 seconds hold)

TESTING COMPOSITE PERFORMANCE

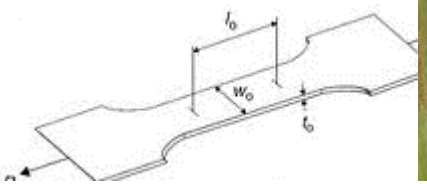
Physical/mechanical properties

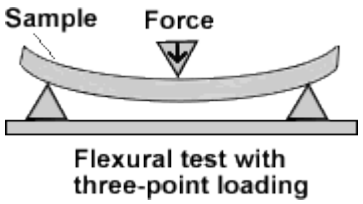
- thermal properties
- tensile strength and modulus
- elongation at break
- flexural strength and modulus
- impact strength
- DMA (Dynamic mechanical analysis)











Flexural test with three-point loading



COB FIBRE TREATMENTS

30% cob fibres in PP (1112Z; Pinnacle Polymers); MFI: 12g/10minutes)

1. Untreated raw fibre



Dark Brown



2. Free phenolics extracted fibre



Brown



3. *p*-Coumeric acid and Ferulic acid extracted fibre



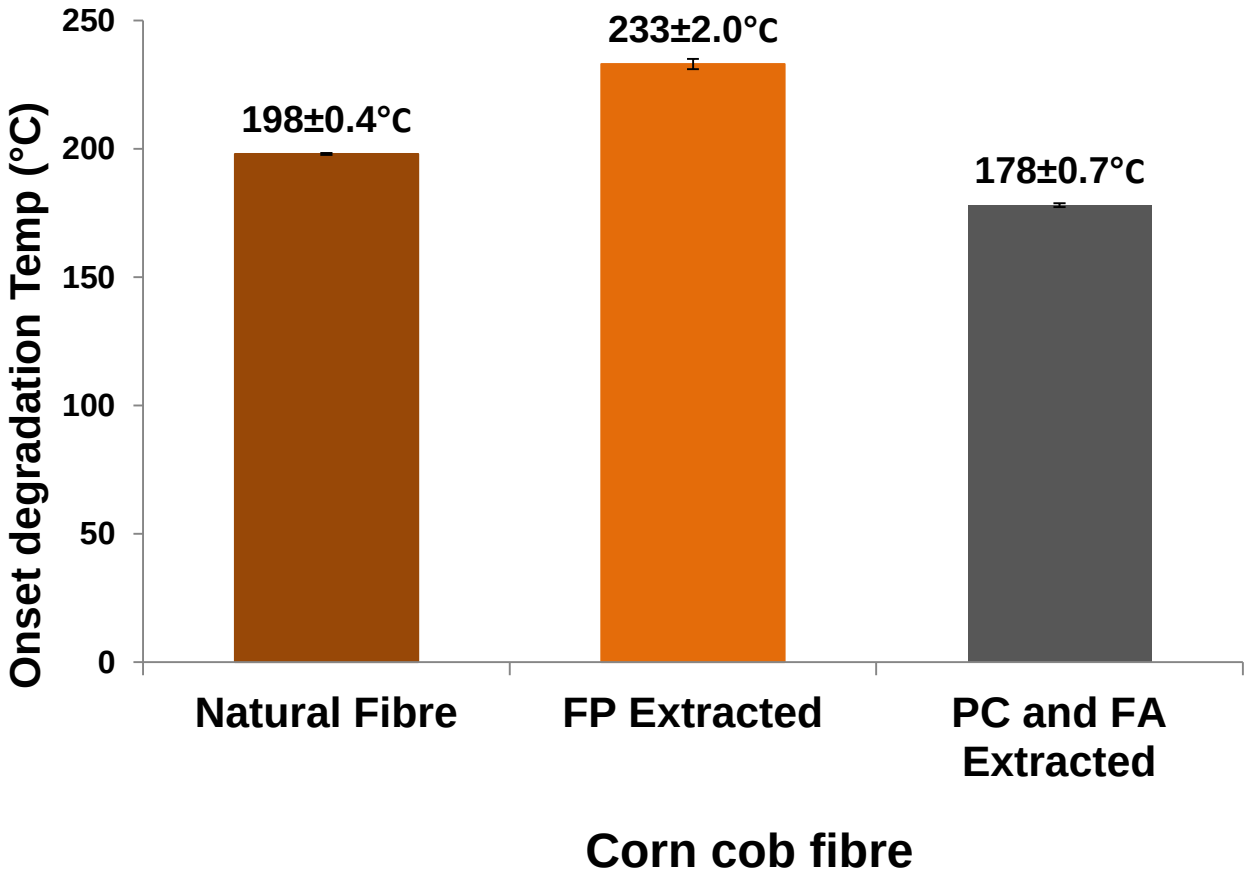
Blackish Brown



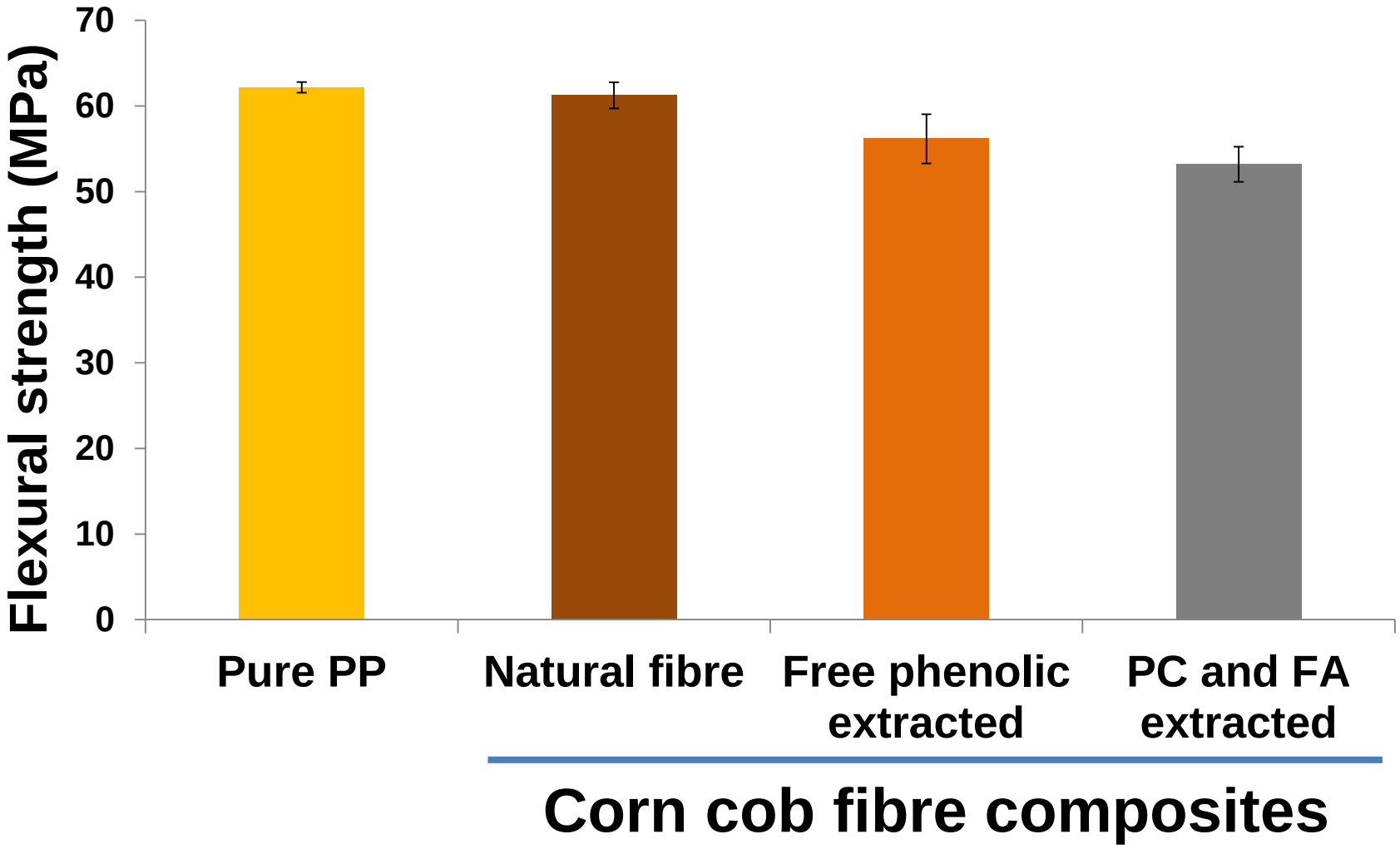
COB FIBRE ONSET DEGRADATION TEMPERATURE (°C)

Fibre Thermal Stability

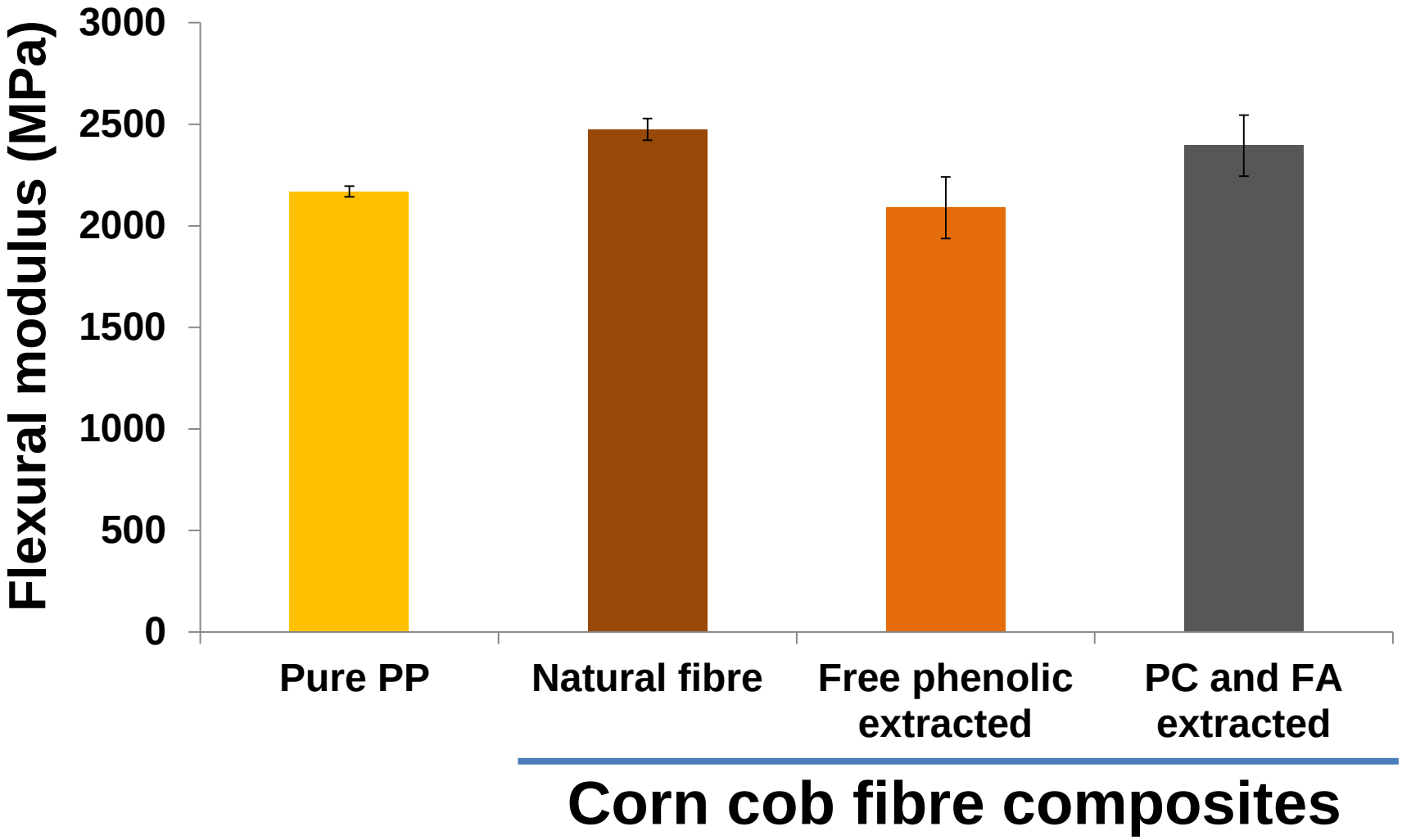
- Fibre weight: ~10 mg
- Temp: 35°C to 700°C @ 20°C min^{-1}
- Condition: Nitrogen@ flow rate of 50 mL min^{-1}
- Onset degradation temperature (ODT): the temperatures (°C) after 150°C at which the sample showed 1% weight loss



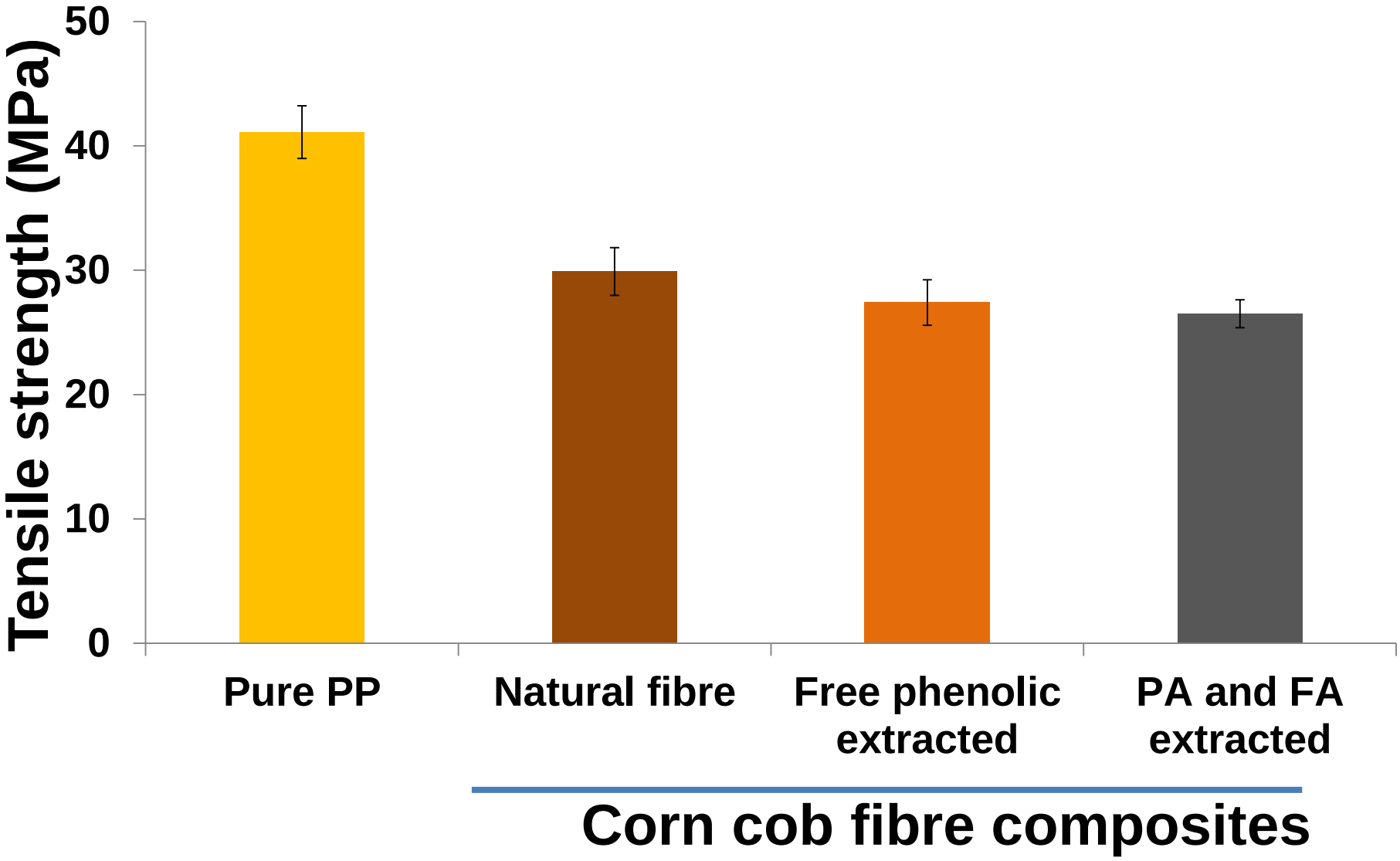
PP/ CORN COB FIBRE COMPOSITE TRAITS - FLEXURAL STRENGTH (MPA) (ASTM D790-10)



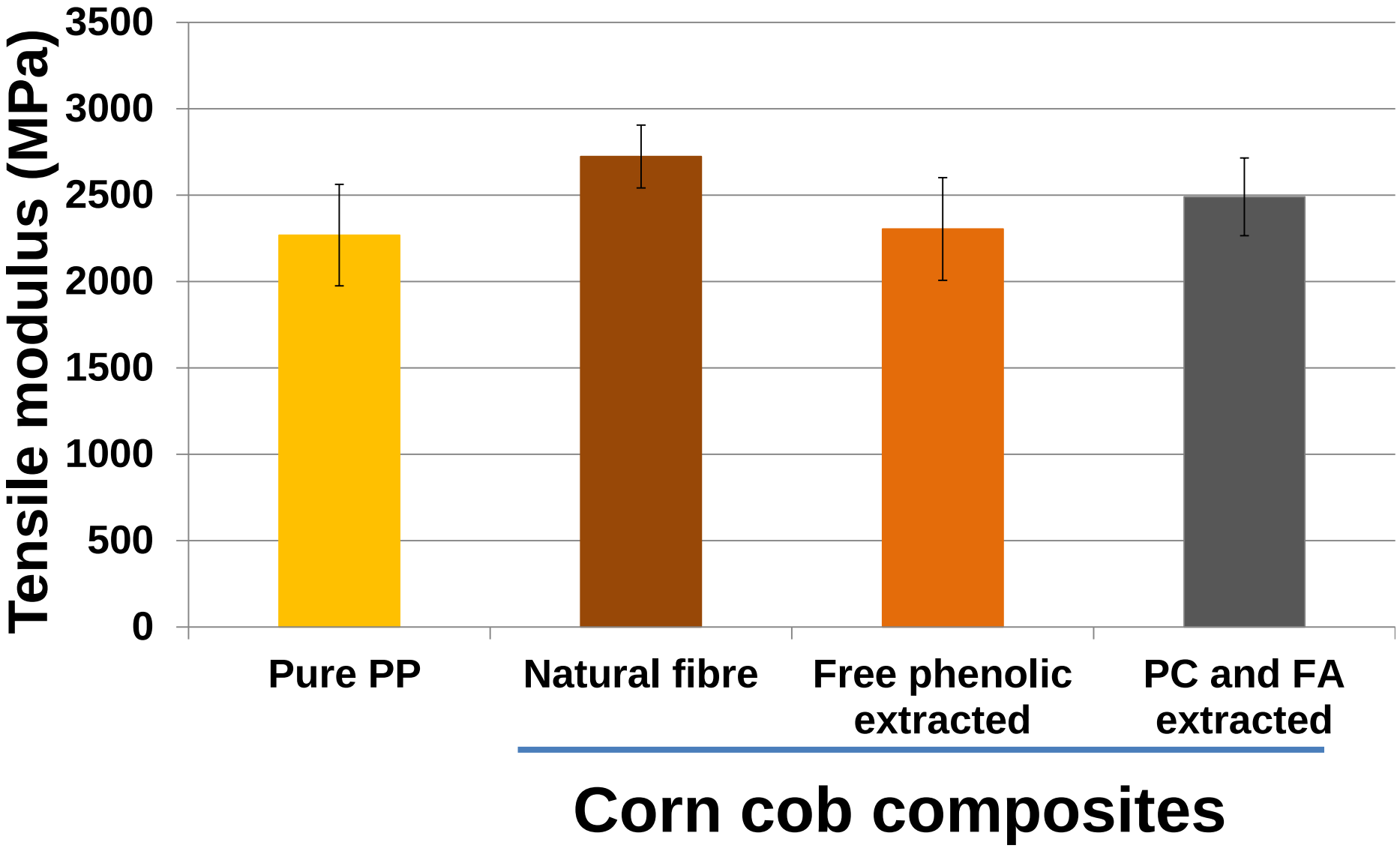
PP/ CORN COB FIBRE COMPOSITE TRAITS - FLEXURAL MODULUS (MPA) (ASTM D790-10)



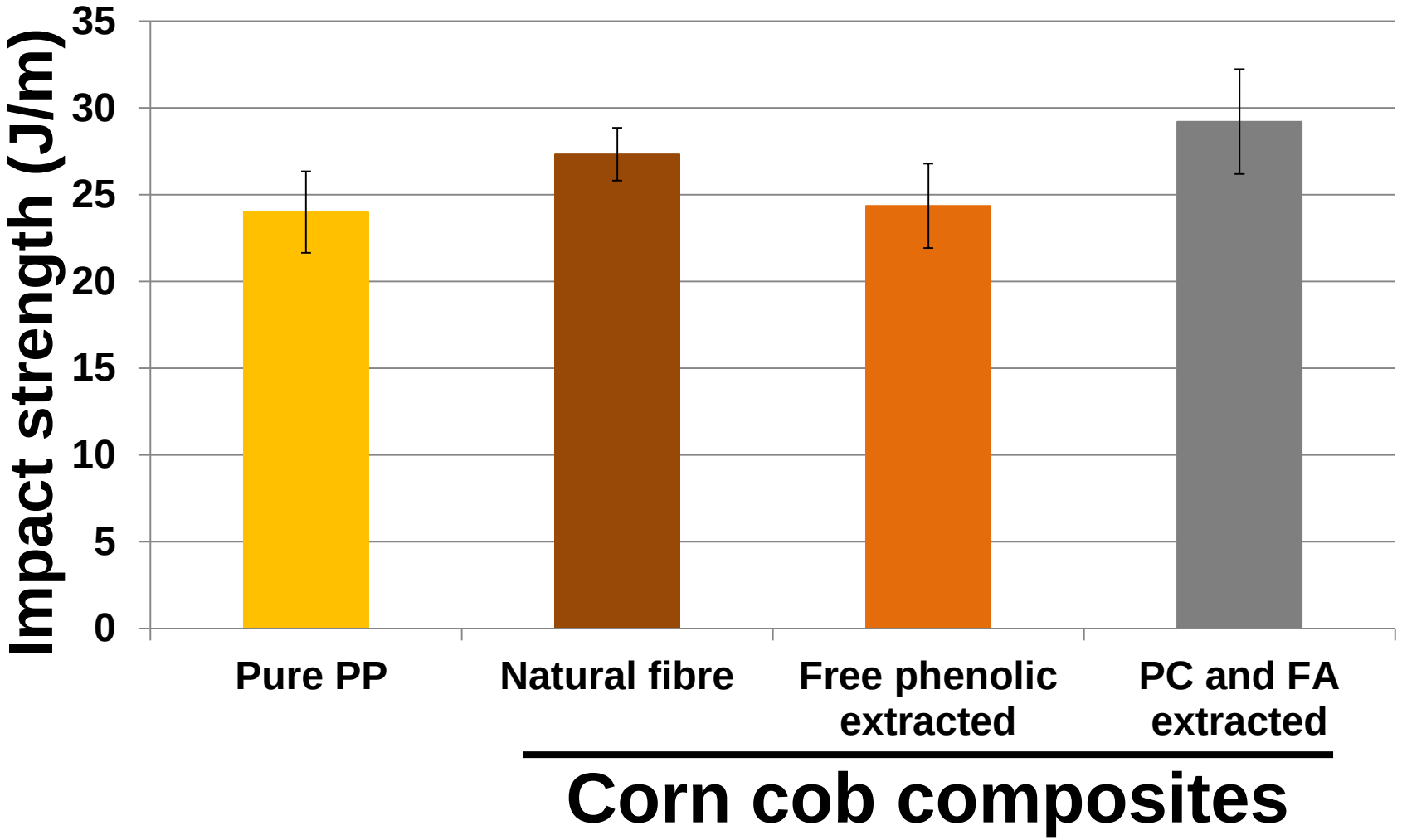
PP/ CORN COB FIBRE COMPOSITE TRAITS – TENSILE STRENGTTH (MPA) (ASTM D638-14 Type IV)



PP/ CORN COB FIBRE COMPOSITE TRAITS – TENSILE MODULUS (MPA) (ASTM D638-14 Type IV)

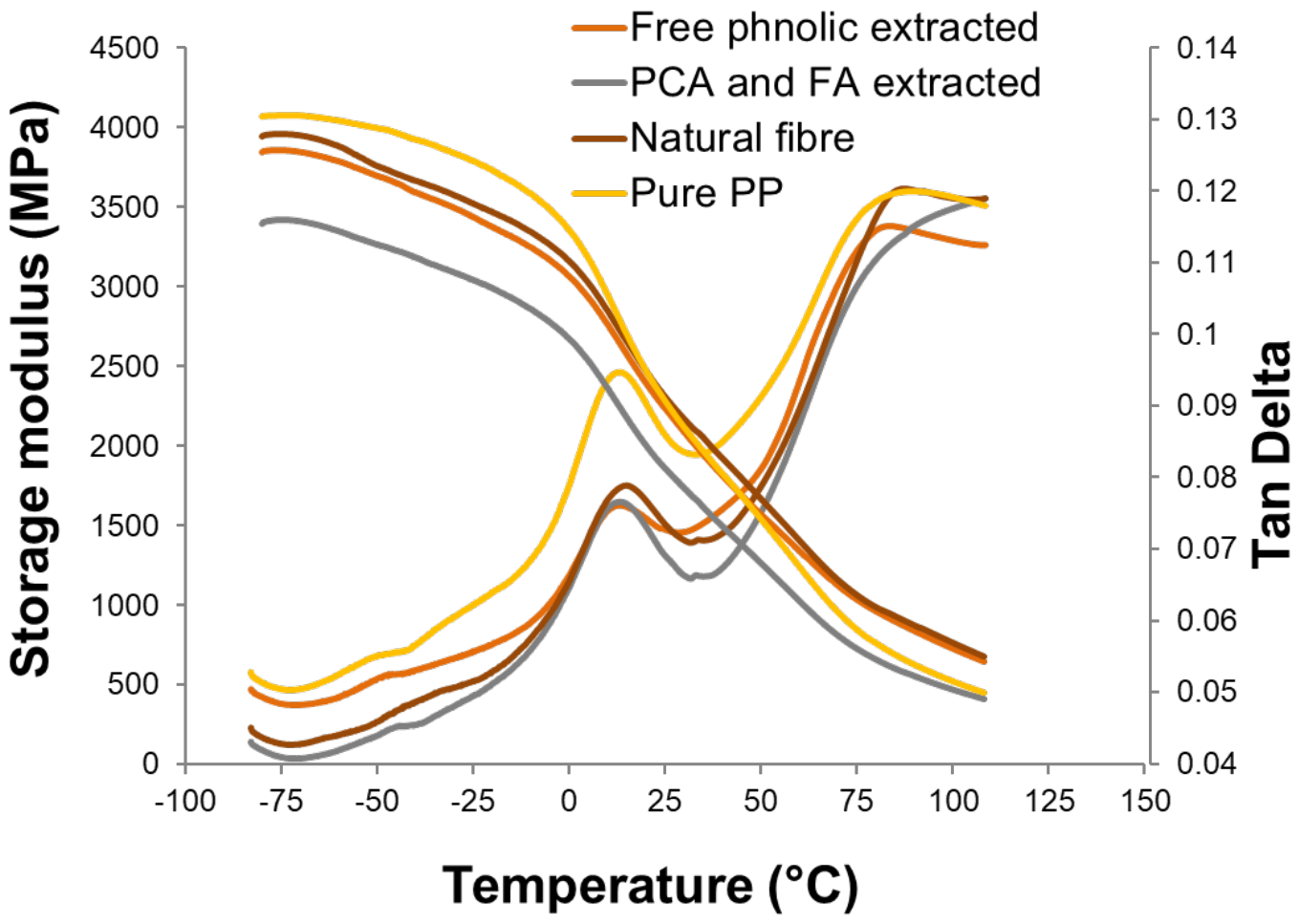


PP/ CORN COB FIBRE COMPOSITE TRAITS – NOTCHED IZOD IMPACT STRENGTH JM-1(ASTM D256)



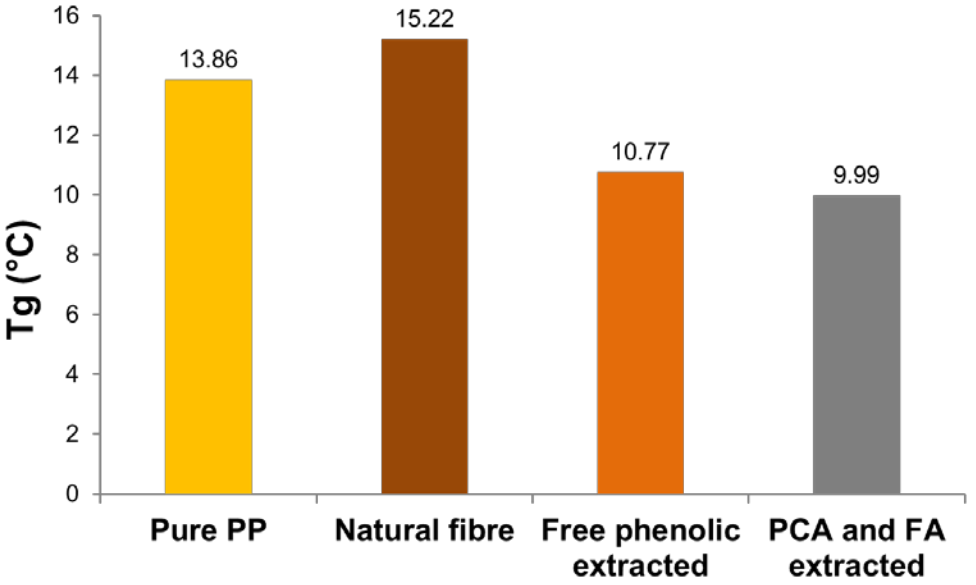
PP/ CORN COB FIBRE COMPOSITE TRAITS – DMA (Dynamic mechanical analysis) of treated fibre composites (3 °C/min, frequency 1 Hz, temperature -80 °C – 110 °C)

- Significant differences in storage modulus between pure polypropylene and composites
- Composites from *p*-Coumaric and ferulic acids extracted fibres had significantly lower storage modulus values than composites from natural fibre and free phenolic extracted fire
- Differences in glass transition temperature among samples observed

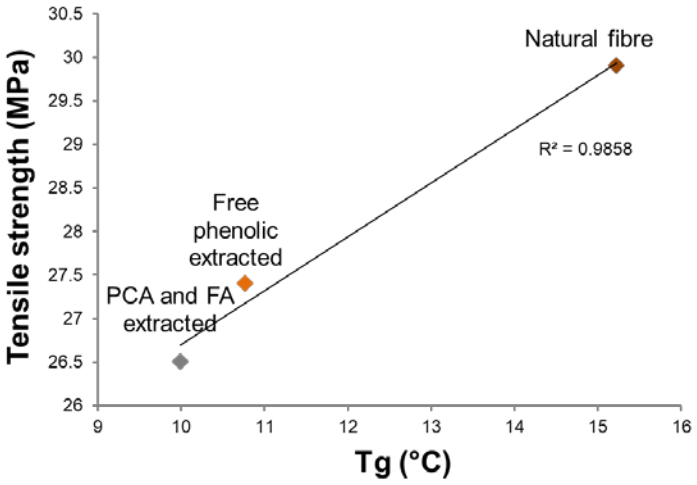


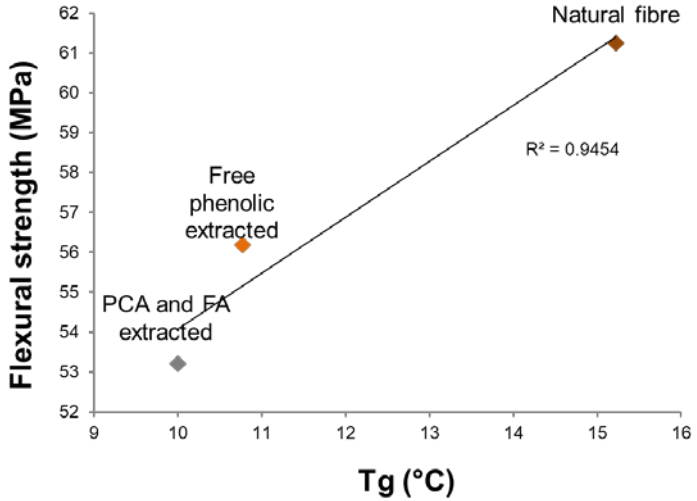
PP/ CORN COB FIBRE COMPOSITE TRAITS – DMA (Dynamic mechanical analysis) of treated fibre composites (3 °C/min, frequency 1 Hz, temperature -80 °C – 110 °C)

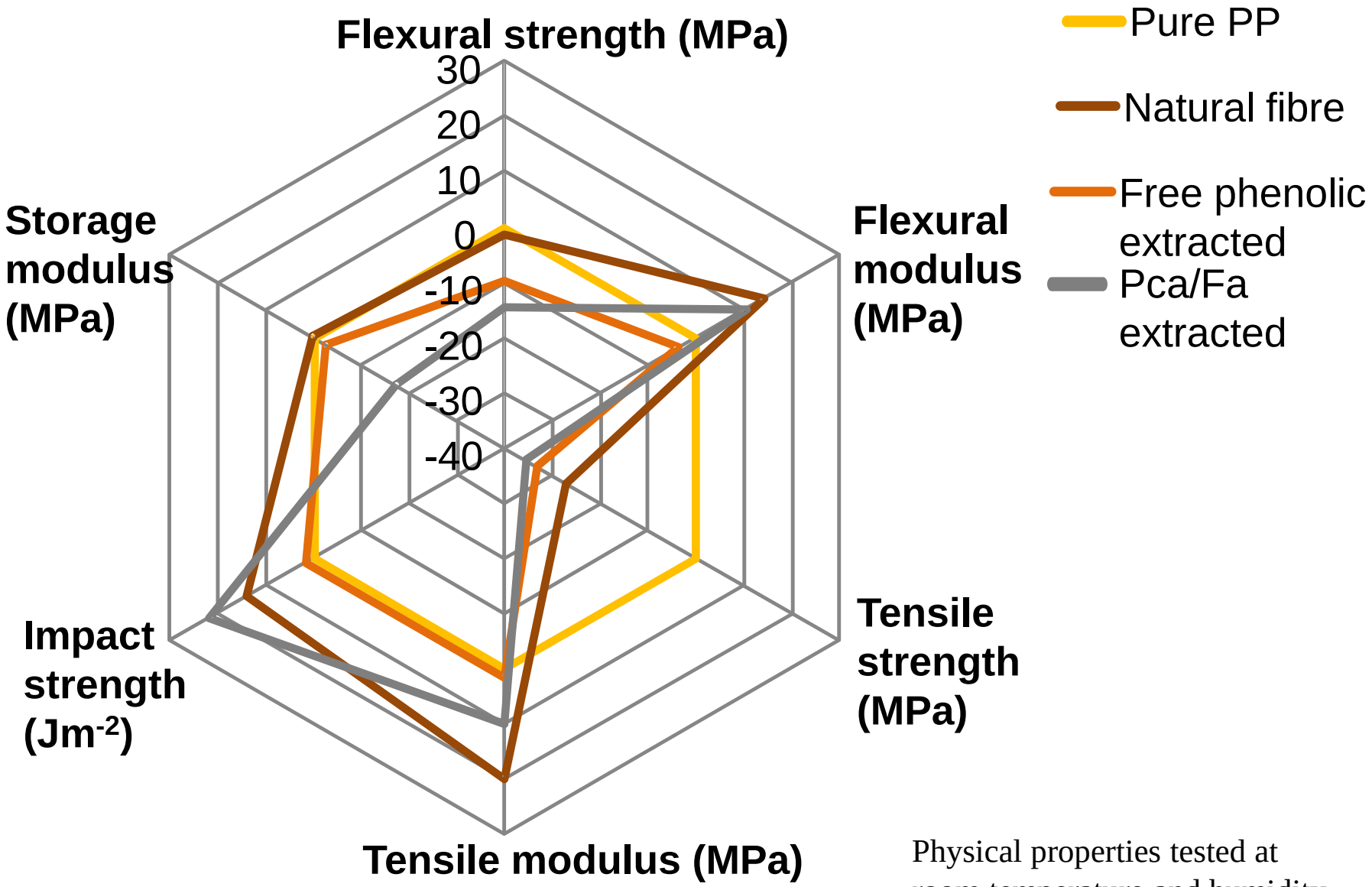
- The glass transition temperature was:
  - higher for the native fibre composite than pure PP
  - lower for the composites prepared from fibres without phenolics



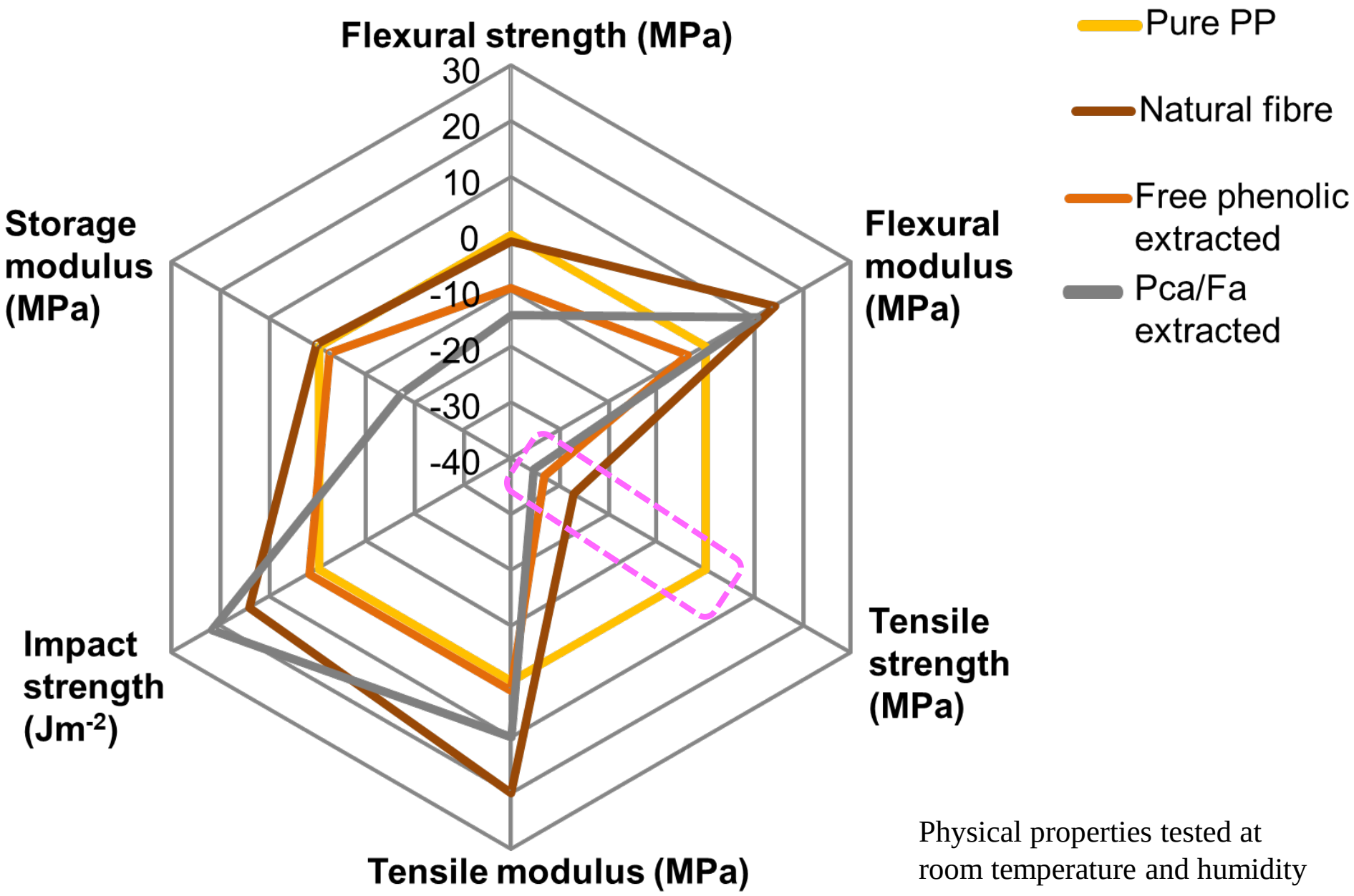
- The glass transition temperature was positively correlated with Tensile strength and Tensile Modulus of the composites



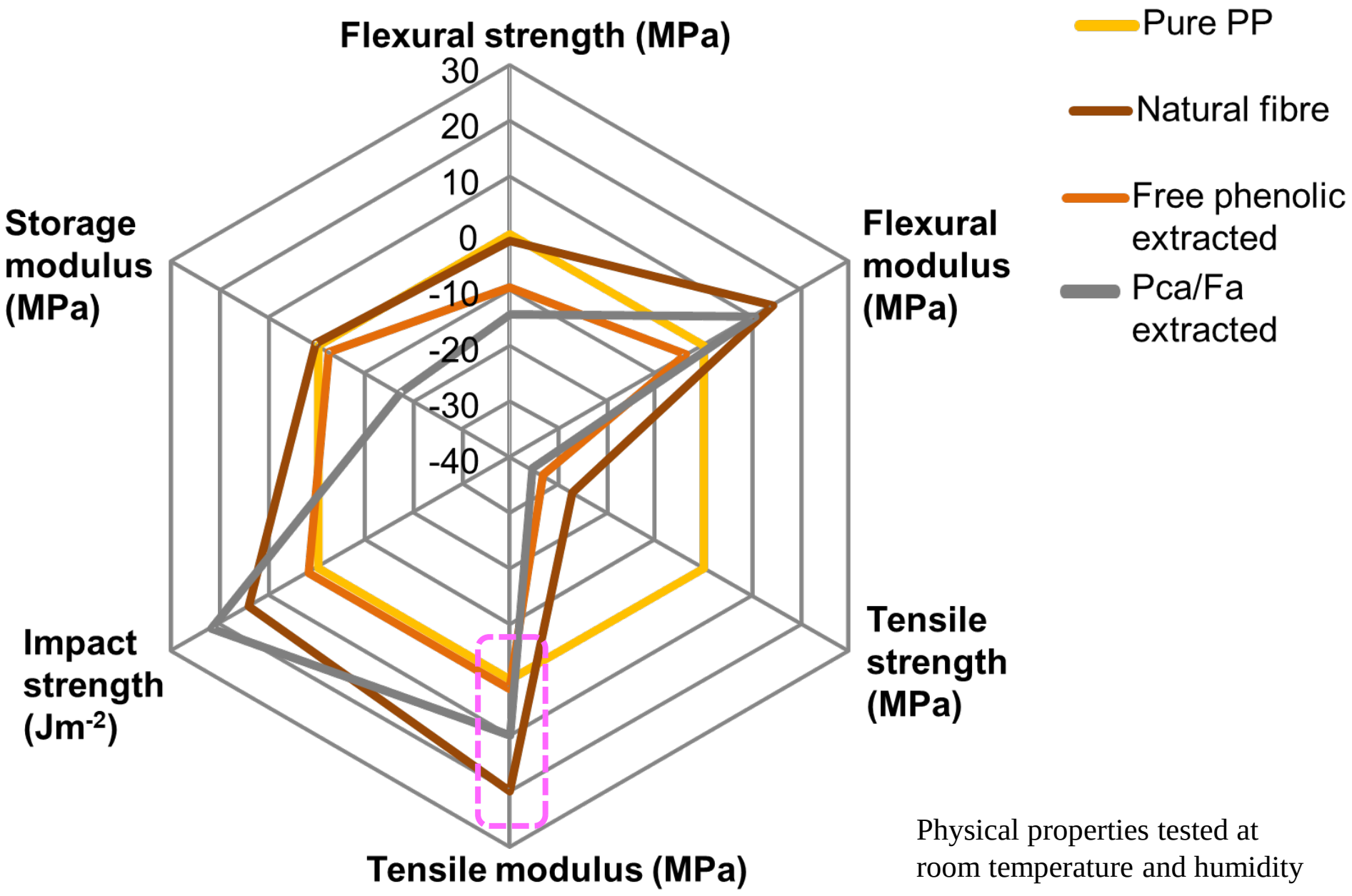




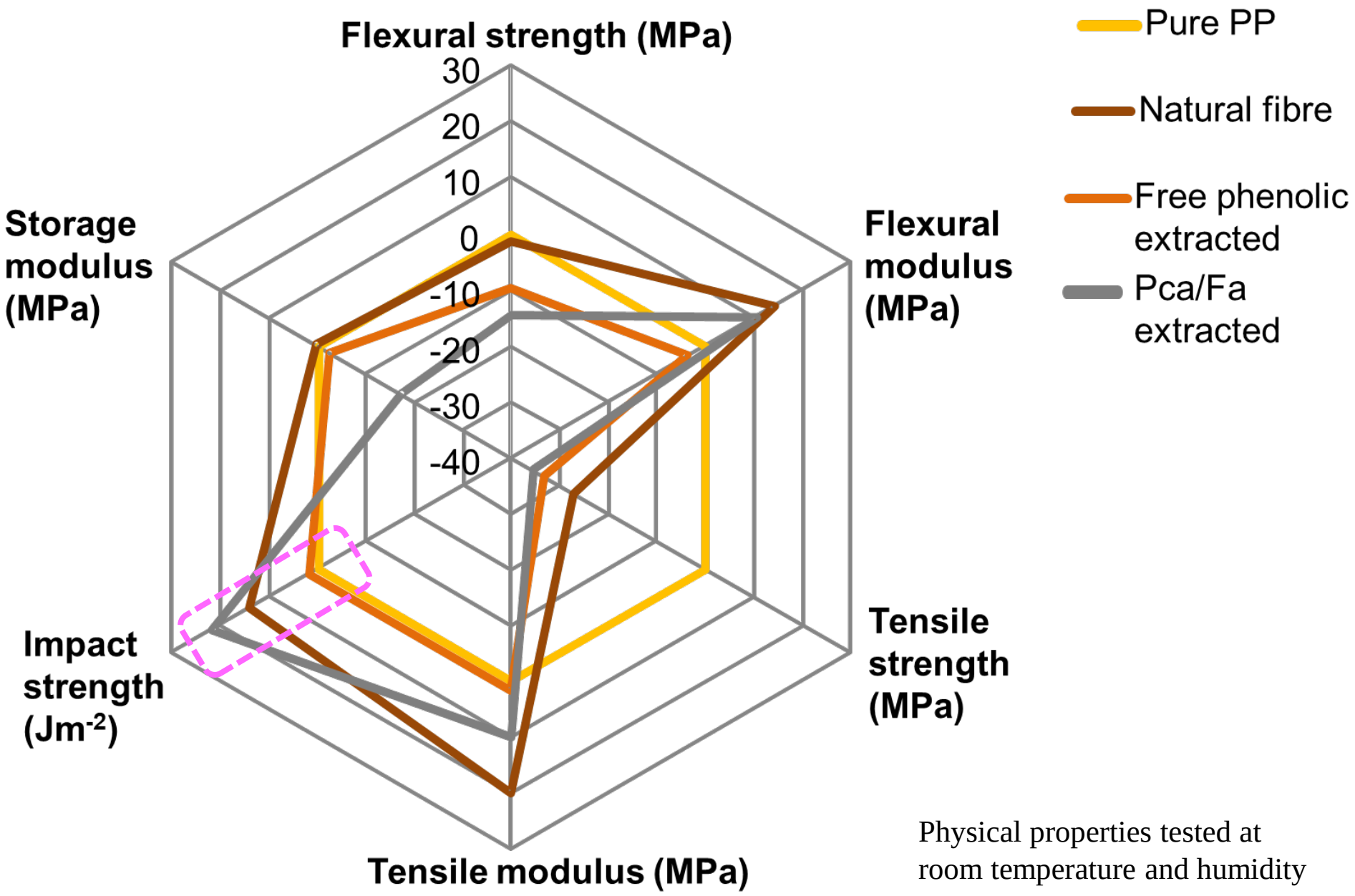
Physical properties tested at room temperature and humidity



Physical properties tested at room temperature and humidity



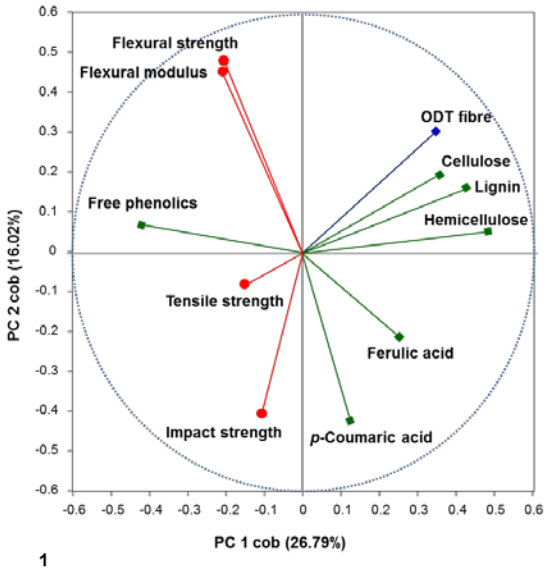
Physical properties tested at room temperature and humidity

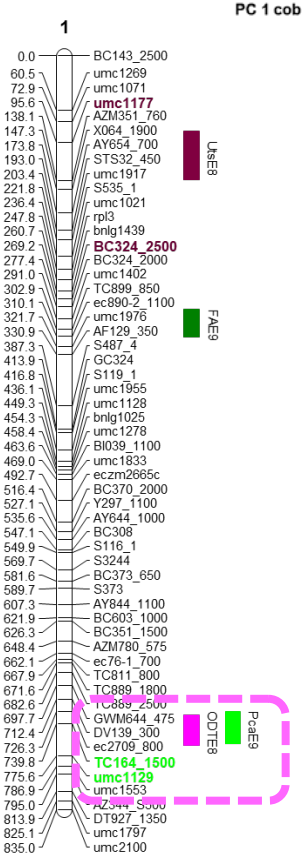


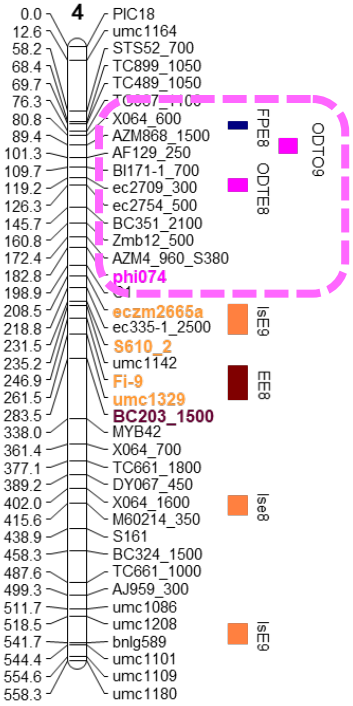
Physical properties tested at room temperature and humidity

SUMMARY

- Removal of phenolics affected the colour of the fibre and composites
- Previous relationships indicating associations between phenolic contents of corn cob fibres and physical properties of composites confirmed, including:
  - Negative association between Free Phenolics (FP) and Onset Degradation Temperature (ODT)
  - Positive association between FP and Tensile Strength (TS)
  - Negative association of p-coumaric acid/ ferulic acid (PCA/FA) on Flexural Modulus (FM)
  - Positive association between FP and Flexural Strength/ Flexural Modulus (FS/FM)
- PCA/FA extracted fibre composites had significantly lower storage modulus values between - 80 to 110 °C







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