Biobased Performance Materials Symposium
15 June 2017, Wageningen, The Netherlands

Session 2
Presentation by: Christian Lenges, *DuPont Industrial BioSciences*

biobased performance materials

Title: **DuPont BioMaterials: Enzymatic polymerization - A new process for engineered polysaccharides**

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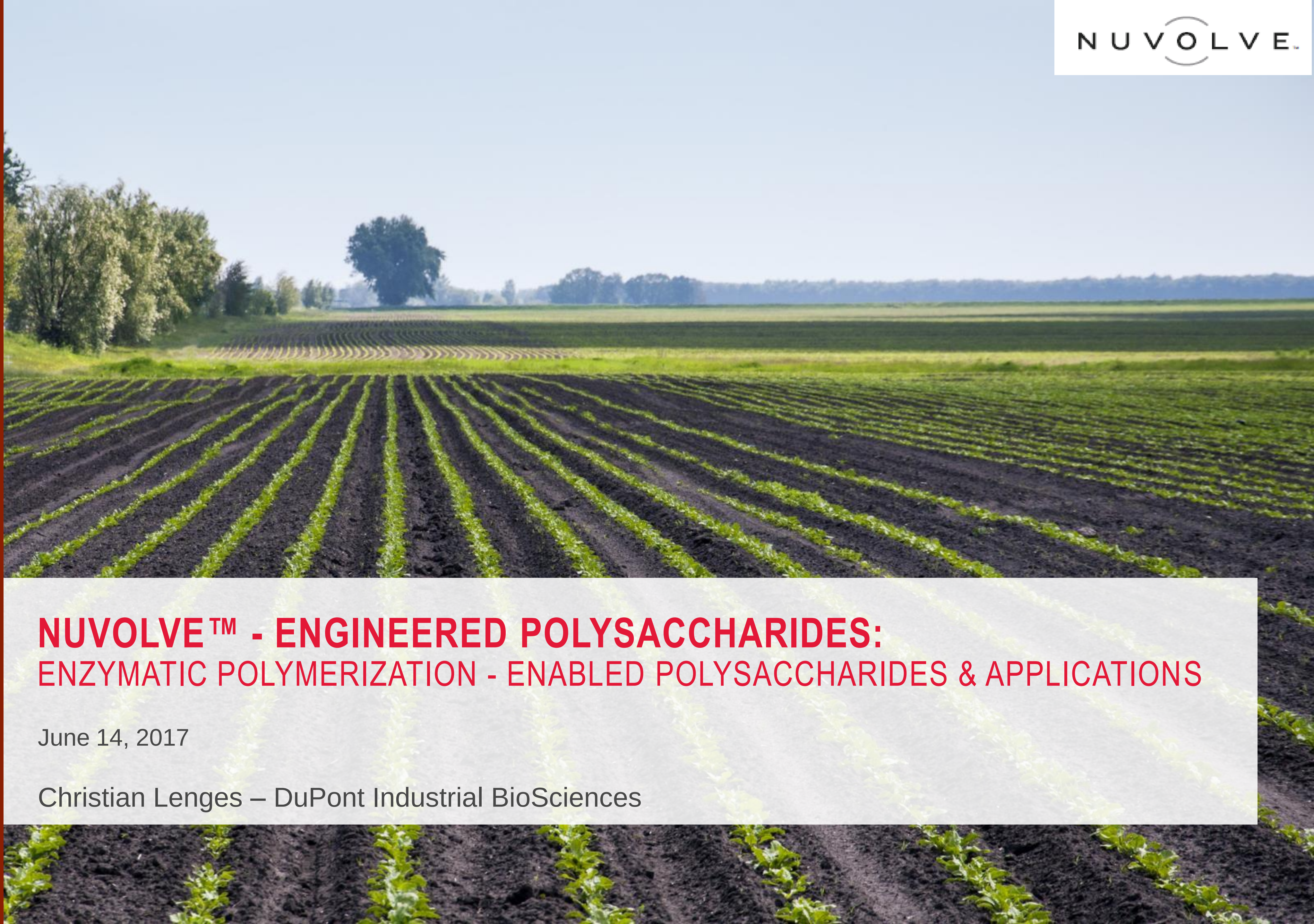
Curriculum:
Christian Lenges, Business Development for BioMaterials in DuPont Industrial BioSciences, focused on the development and launch of growth businesses to make industrially important chemicals and materials from renewable feedstocks. He has experience in a variety of businesses and functions in DuPont including product & technology development, portfolio management & venture leadership. He has had leadership roles in DuPont's efforts in Biomaterials since 2008 in the Sorona® business, and in the biomaterial ventures driving towards commercial launch.

Dr. Lenges holds a Diplom Degree from the Heinrich Heine University in Duesseldorf, and a Ph.D. in Chemistry & Catalysis from the University of North Carolina at Chapel Hill.

Abstract:
DuPont Industrial BioSciences continues to lead the BioMaterials space by advancing the development of new material platforms with differentiated performance and unique customer value. Selecting winning project propositions and managing the complex path from proof of concept demonstration to commercial launch has been key to creating growth in the biomaterials space. Within this presentation, one program in the development portfolio will be discussed in more detail.

Polysaccharides are important biopolymers with a wide range of industrial and consumer product applications. Historically, structural polysaccharides such as cellulose have been the backbone of early material science for applications in fibers, films and early thermoplastics. DuPont Industrial Biosciences has developed a family of engineered polysaccharides ranging in molecular weights, solubility, and polymer architecture. The underlying enzymatic polymerization process offers the opportunity to design the polymer structure and the material properties of these new biomaterials.



NUVOLVE™ - ENGINEERED POLYSACCHARIDES:
ENZYMATIC POLYMERIZATION - ENABLED POLYSACCHARIDES & APPLICATIONS

June 14, 2017

Christian Lenges – DuPont Industrial BioSciences

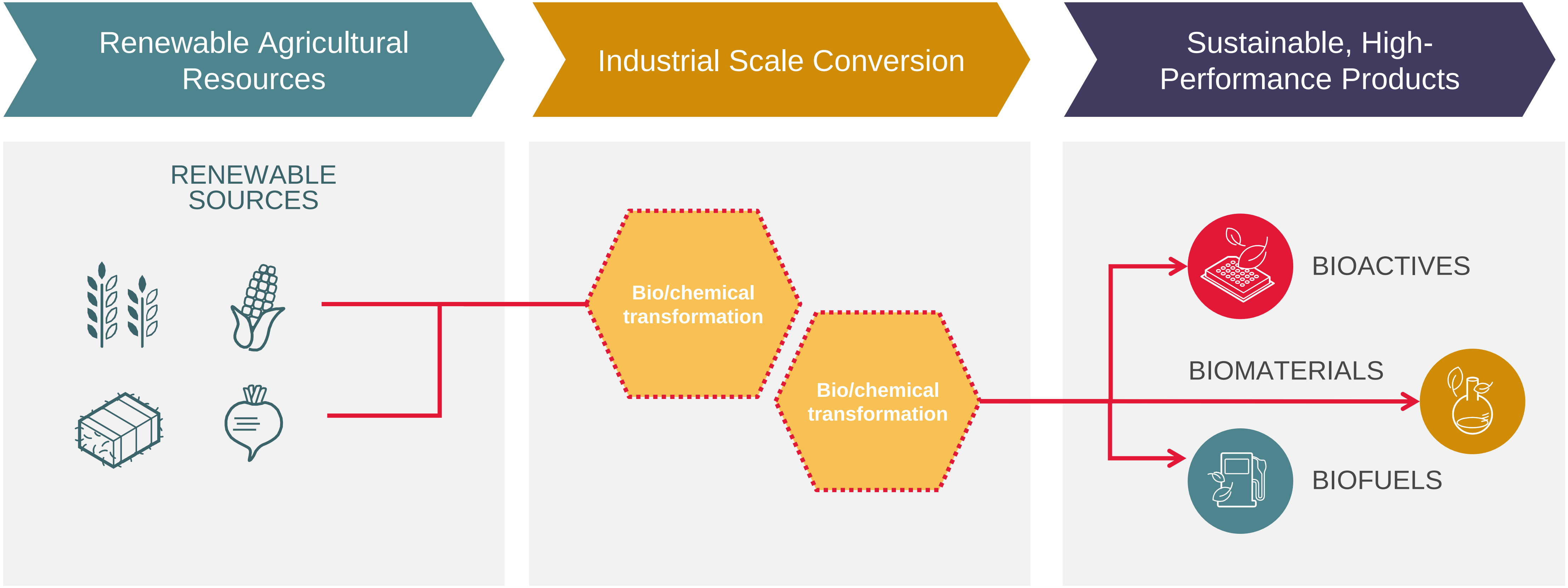
RETHINK RENEWABLE PERFORMANCE

DuPont Biomaterials ***takes cues from nature*** **to create eco-efficient renewable biomaterials that enhance the performance of everyday products**

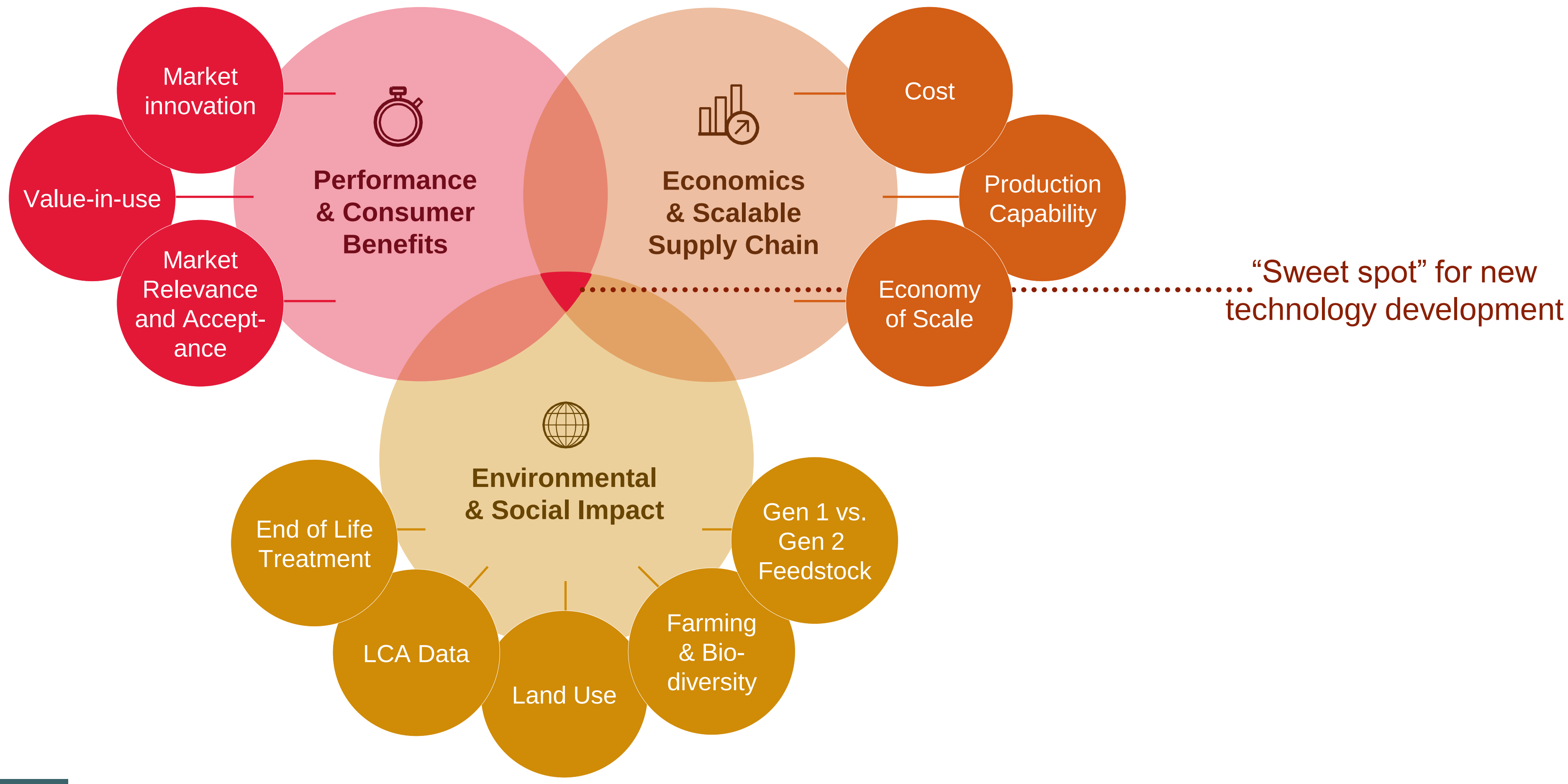
INNOVATIVE SCIENCE	SCALABLE SUPPLY	RENEWABLE SOURCING
↓	↓	↓
HIGH PERFORMANCE	ACCESSIBLE & AFFORDABLE	RESPONSIBLE BIOMATERIALS

ADVANCING THE FUTURE OF INDUSTRY TO SERVE SOCIETY AND SAFEGUARD THE ENVIRONMENT

DuPont Industrial Biosciences is working to reform the way we produce and consume



We consider a range of important, inter-connected factors when developing new biomaterials technology

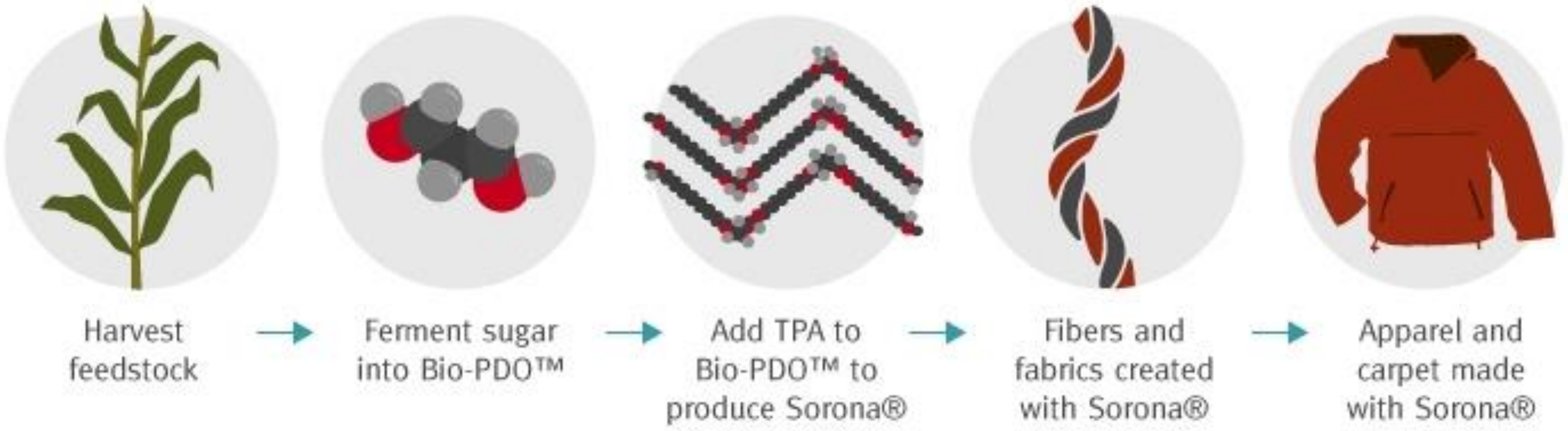





Sources Matter




THE STORY OF SORONA



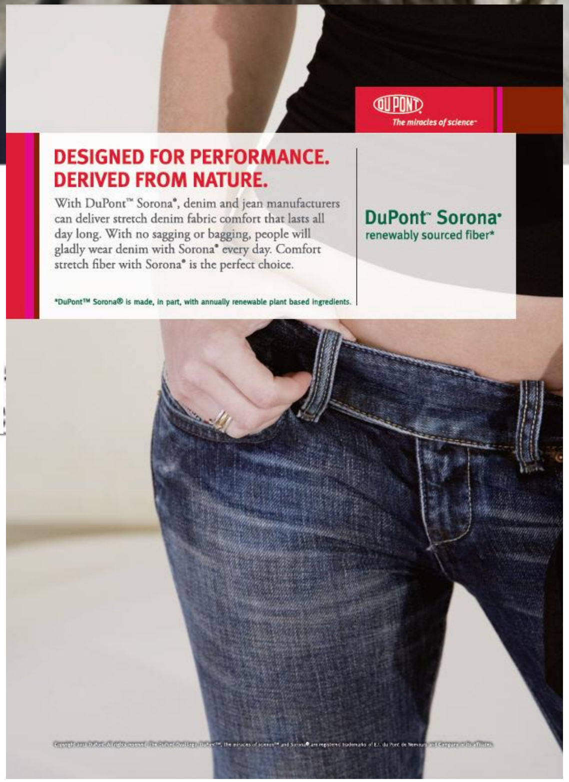
Sorona® is made, in part, with annually renewable plant-based ingredients.

DISCOVER THE FEELING

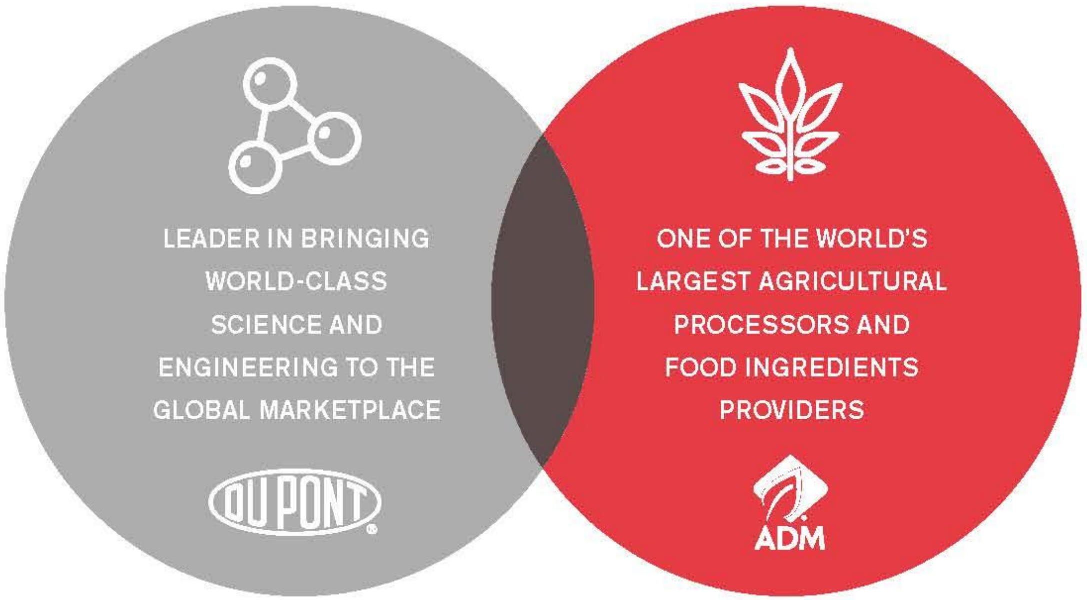
Developed in part from renewably sourced plant materials, every Sorona fiber is designed to make yarn feel softer and work harder, changing what's possible with textiles. From a beautifully vibrant and durable carpet to exceptionally soft and flexible yoga wear, Sorona can make any textile **look good, feel good and do good.**

SOR
ONA®

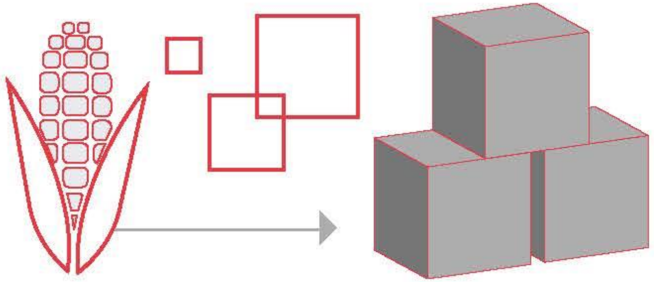
DUPONT™
sorona®



A REVOLUTIONARY PARTNERSHIP = FDME BREAKTHROUGH

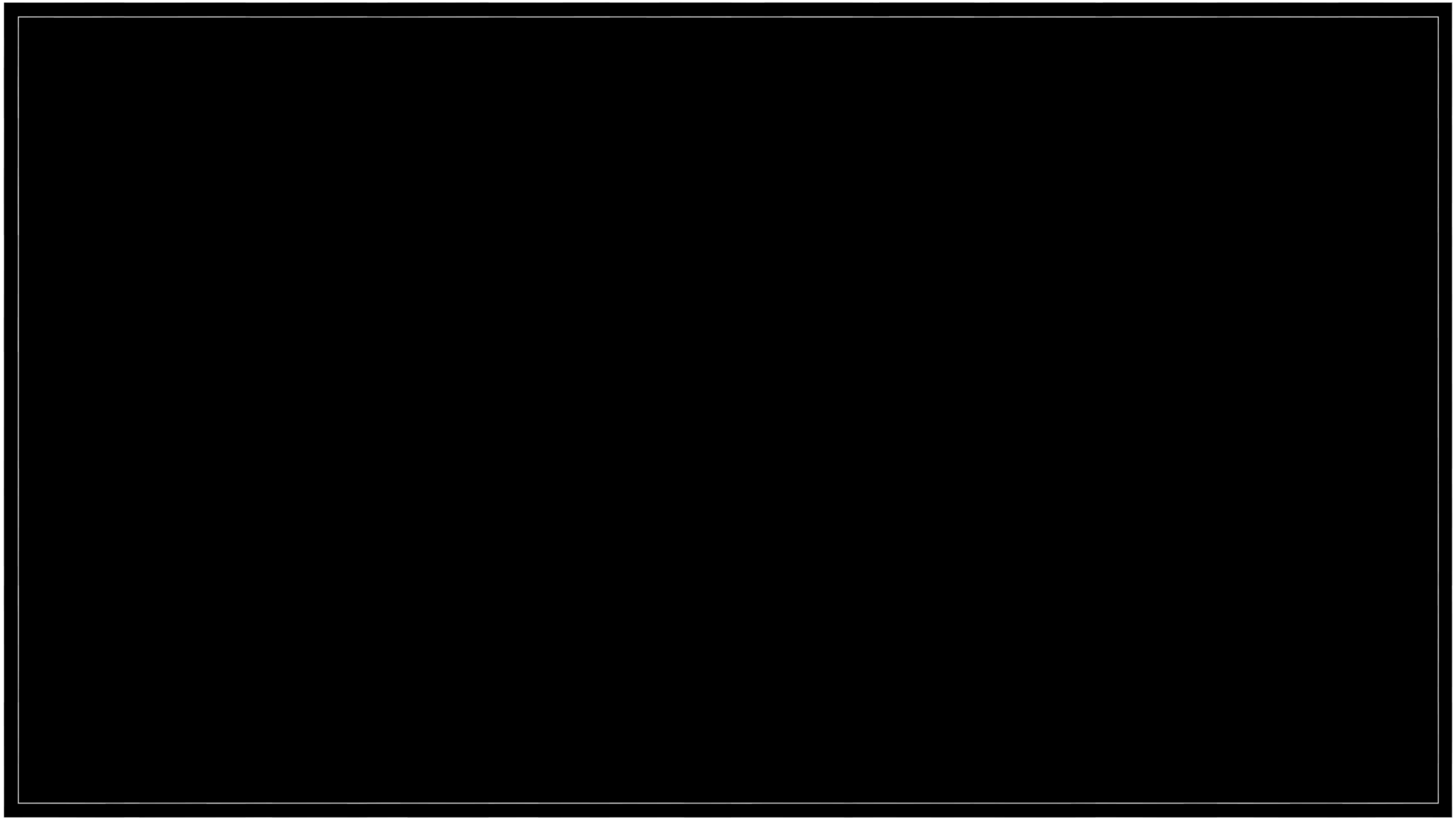


With their combined expertise in agriculture and food science, the two companies developed an innovative new process for turning fructose into biomaterial – specifically, the molecule furan dicarboxylic methyl ester (FDME) – a building-block that can be converted into a number of high-value, bio-based chemicals or materials.



THIS SCIENTIFIC BREAKTHROUGH OPENS THE DOOR TO NEW POLYMER GROUPS AND HAS CREATED A MORE EFFICIENT, ECONOMICALLY VIABLE PROCESS.

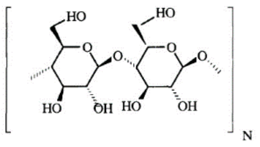
THE NEXT BREAKTHROUGH IN BIOMATERIALS: LEARNING FROM NATURE



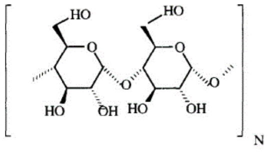
INSPIRED BY NATURE

Polysaccharides extracted from plants are widely used to provide unique end-use applications but are limited by processes and raw material source. Nature often produces mixtures.

Cellulose
β(1,4) linkage



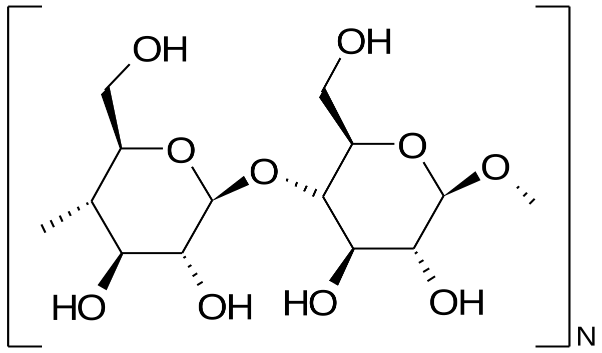
Starch
α(1,4) linkage



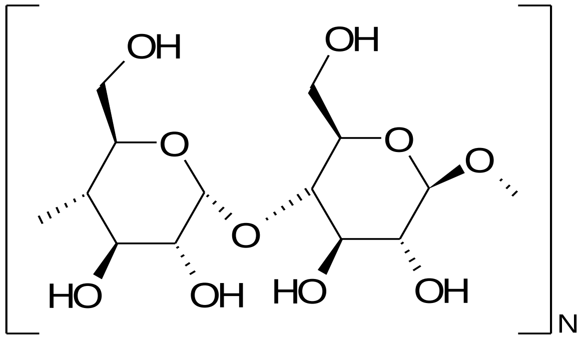
BIOMATERIAL PLATFORM INSPIRED BY NATURE

Cellulose and starch are well known building blocks for natural based materials.

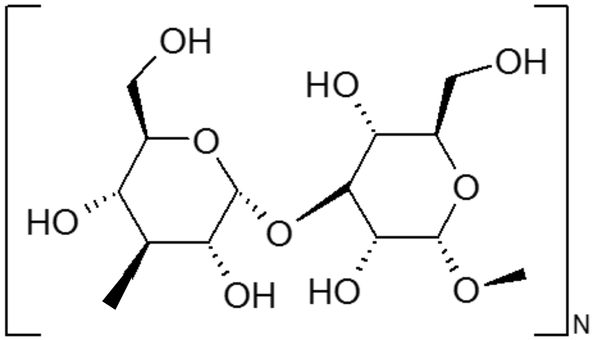
Alpha-1,3-glucan is a largely unexplored structural polysaccharide.



Cellulose: beta (1,4) linkage



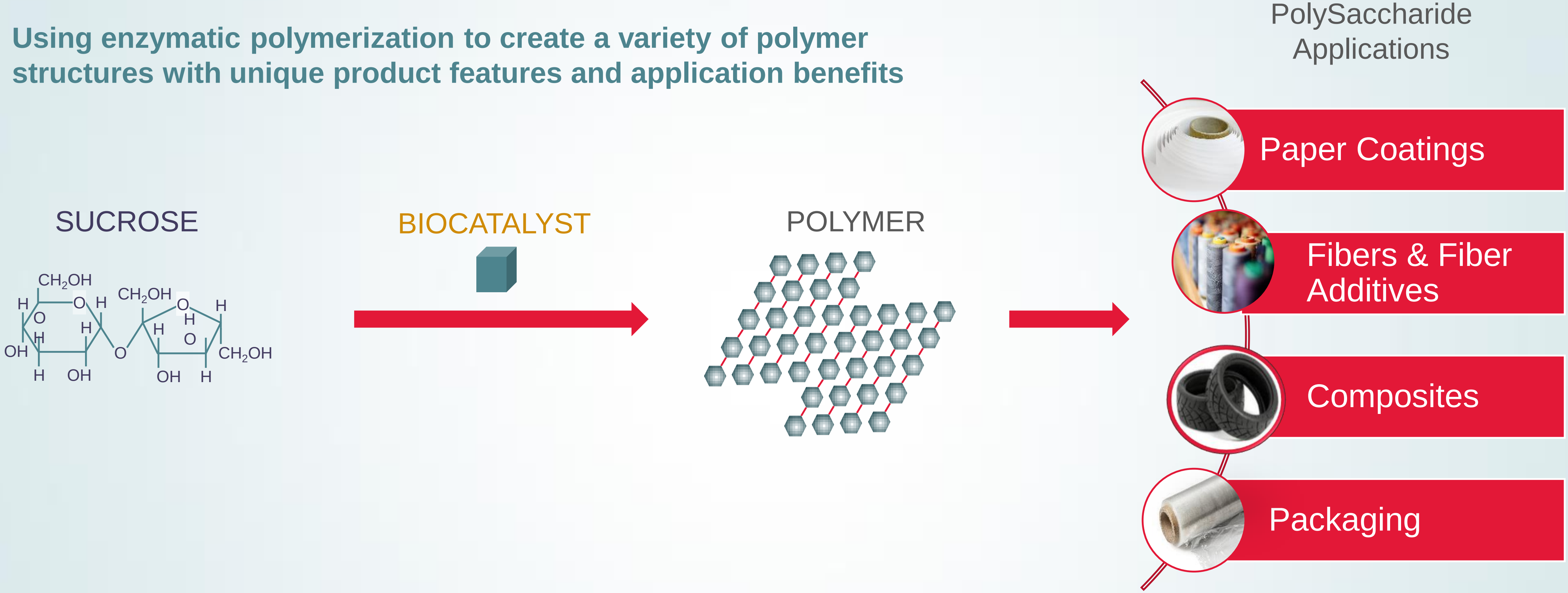
Starch: alpha (1,4) linkage



alpha (1,3) linkage
Engineered Polysaccharide

ENGINEERED POLYMERS DIRECTLY FROM SUGAR

Using enzymatic polymerization to create a variety of polymer structures with unique product features and application benefits



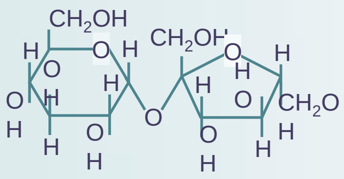
- Linkage control: Selective polymerization of sucrose to polysaccharide
- Structural control: Crystallinity, solubility – DPW & PDI Control
- Process control to define polymer microstructure

NUVOLVE

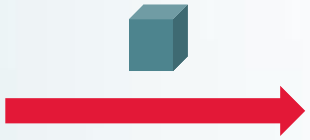
BIOPROCESS CONTROL: FROM MOLECULAR DESIGN TO POLYMER ARCHITECTURE & PARTICLE MORPHOLOGY

Platform Technology to Engineer New Raw Materials

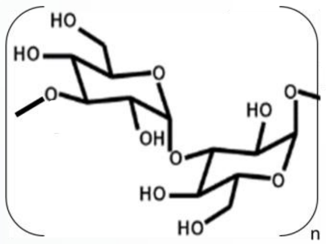
SUCROSE



ENZYMATIC POLYMERIZATION

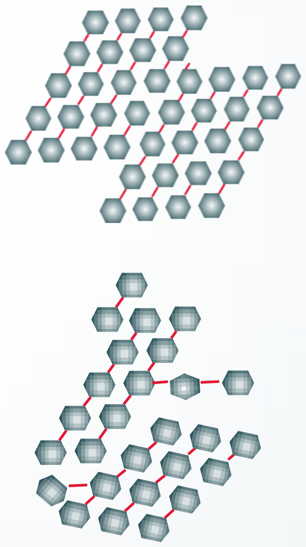


MOLECULAR DESIGN



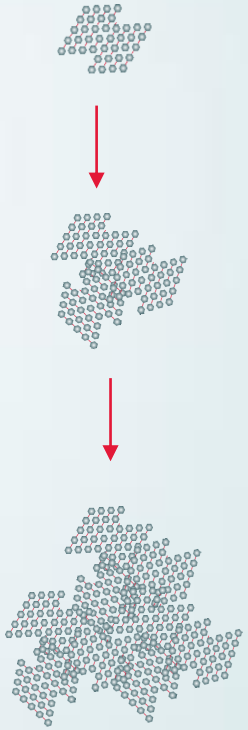
Linkage Control
Selective Functionalization

POLYMER ARCHITECTURE



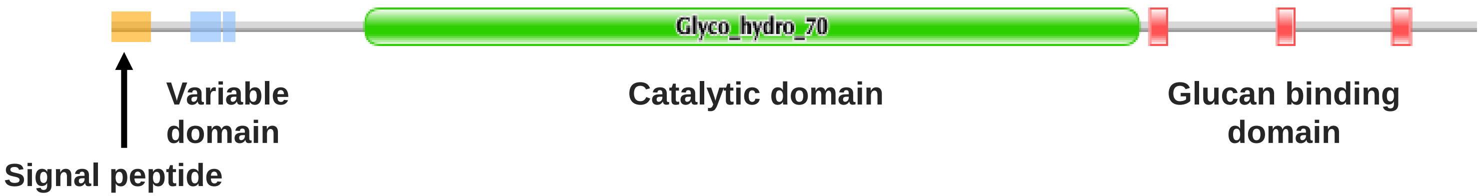
Linear vs Branched
Structures

MATERIAL MORPHOLOGY

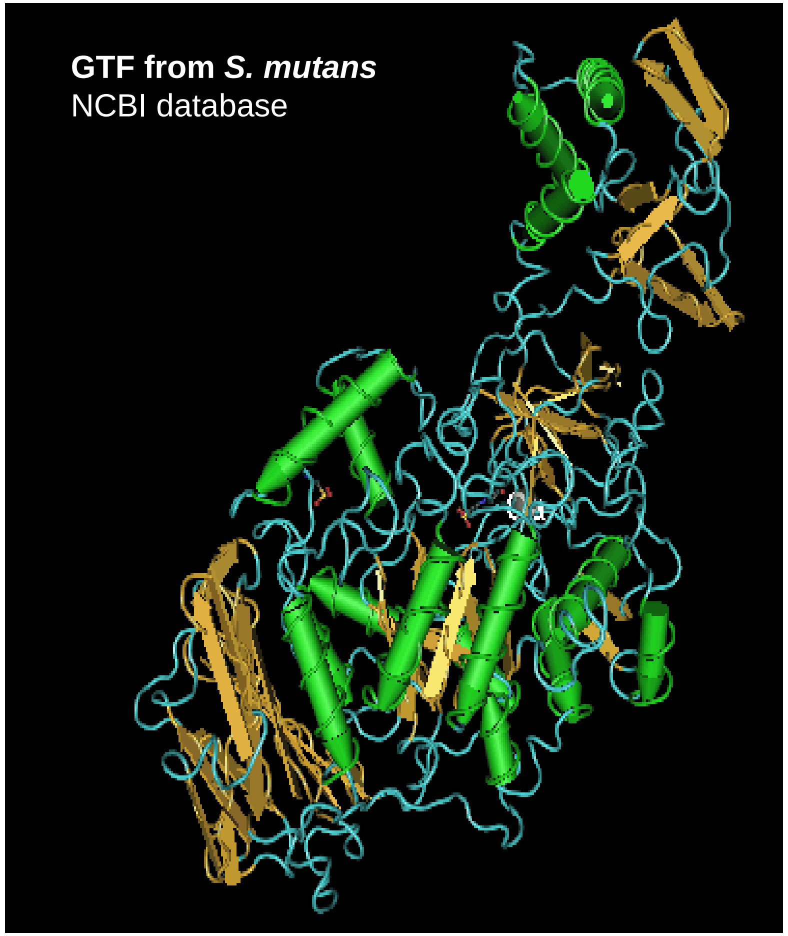


BIOCATALYST – GLUCOSYLTRANSFERASE (GTF)

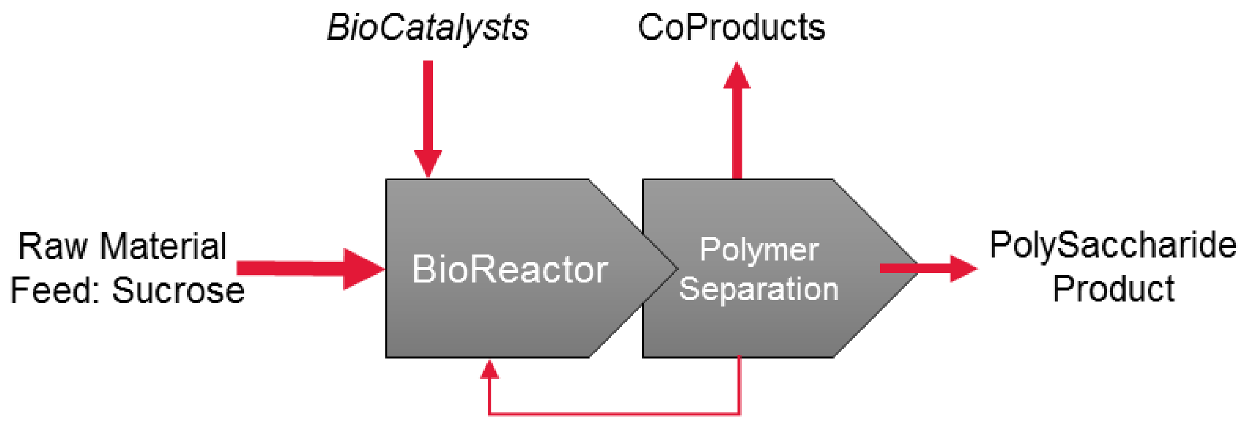
Highly conserved structure despite significant sequence diversity



- Glycoside-Hydrolase family 70 (GH70)
- Monomer with typical MW of 160 kDa
- Extracellular enzymes, mainly produced by:
  - Streptococcus species
  - Leuconostoc species
  - Lactobacillus species



NUVOLVE™ ENGINEERED POLYSACCHARIDES PATH TO COMMERCIAL REALITY



Engineered PolySaccharide BioProcess

Key Status Highlights

- Advancing process, product & application development
- Targeting first commercial scale supply
- Ongoing pilot plant operations to supply first sales
- Development materials available

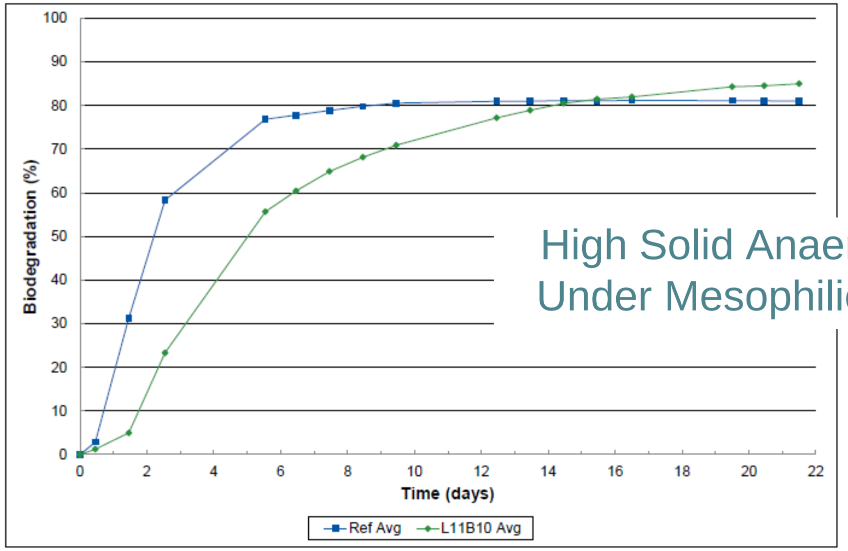
POLYSACCHARIDE BASIC PROPERTIES – ALPHA 1,3-GLUCAN

- Water insoluble free flowing powder
- Zeta Potential essentially zero !
- Water absorption isotherm between cellulose I & II

Typical Properties	
Brightness	90 - 96
Degree of Polymerization	800 (400 – 1500)
PDI	1.7 - 2
Residual Sugars	0.1-1.0 wt%
Dry polymer solids	> 88 wt%
Particle size distribution (d50)	10-30 µm
Primary Particle Size	10 – 30 nm
Overall Surface Energy	53 mJ/m2
Crystallinity Index	~ 50%
Bulk Density	1.5 kg/m3

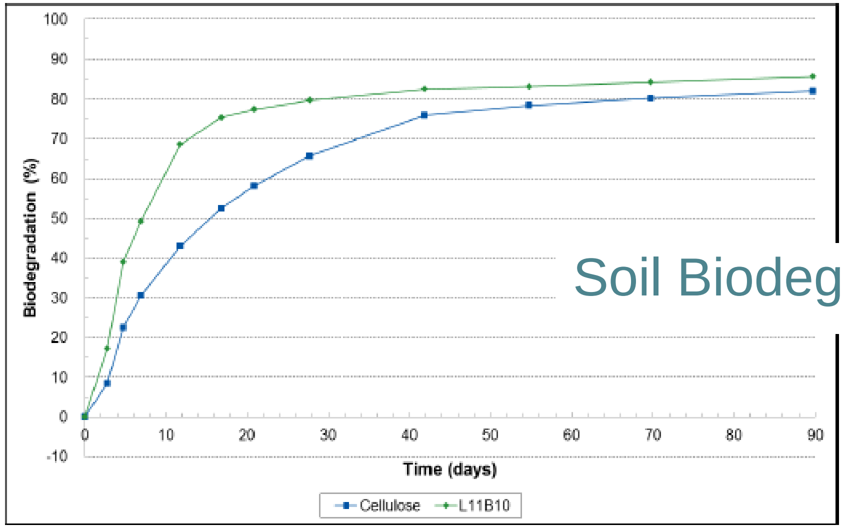
BIODEGRADABILITY ASSESSMENTS

- ASTM D5511: simulates & accelerates biodegradation process in landfill
- Final biodegradation was 85% +/-1.0% or 105.0% relative to reference cellulose
- Conclusion: Considered completely biodegradable under mesophilic anaerobic conditions.



High Solid Anaerobic Degradation Under Mesophilic Conditions (37C)

- ISO 17556 Plastics: determines ultimate aerobic biodegradability in soil
- Final biodegradation was 85.6% +/- 0.3% or 104.4% relative to reference cellulose
- Conclusion: Fulfilled 90% requirement within 90 days of testing under given aerobic conditions.



Soil Biodegradation Test

POLYSACCHARIDE IN BIOCOMPOSITE APPLICATION EXAMPLES

Engineered polysaccharides from DuPont show promising performance results across multiple markets & applications. For example:

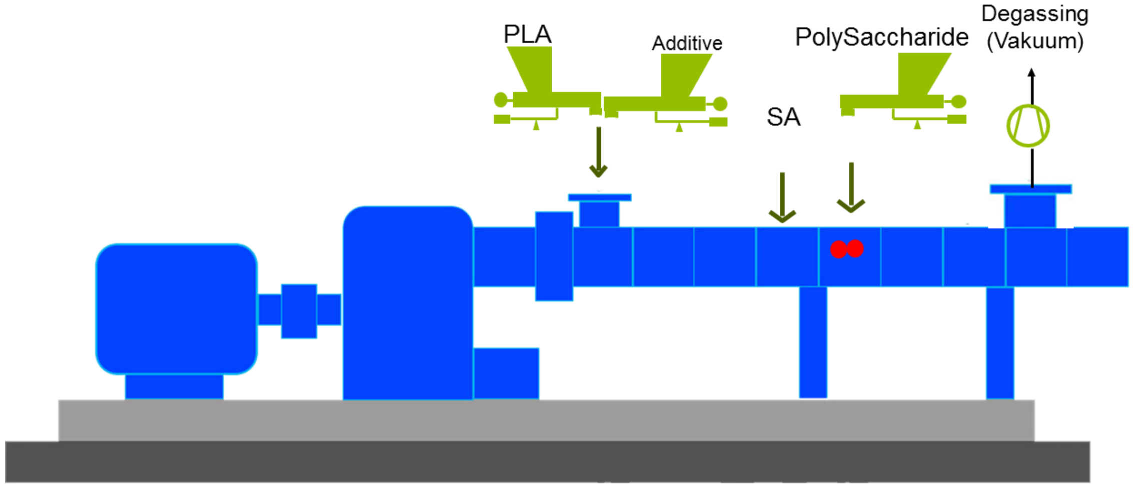
THERMOPLASTIC COMPOSITES

RUBBER COMPOSITES

HIGH SPEED INK JET COATINGS

THERMOPLASTIC FILLER APPLICATIONS

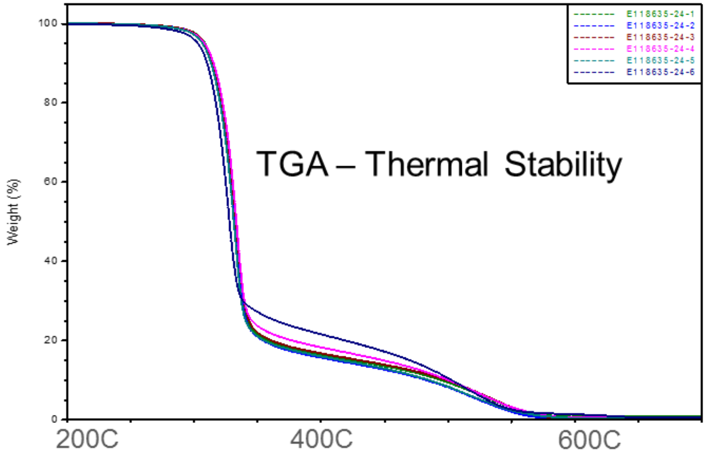
- Spherical Particle in Powder Form (5-10 micron)
- Efficiently Compounded into PP, PE, PLA, others



- Maintains Mechanical Properties of Compounds at high PolySaccharide load
- Example 10% - 40% additive in PLA:
  - Tensile Modulus: 4000 +/- 500 [MPa]
  - Tensile Strength: 40 +/- 10 [MPa]

- Whiteness & Low impurities
- Thermal Stability
  - Less degradation byproducts
  - Low melt viscosity - even at high loads

Polysaccharide %	MFR 230C
0	35
10	24
20	22
30	21
40	20
50	18



PLA / POLYSACCHARIDE COMPOUNDS

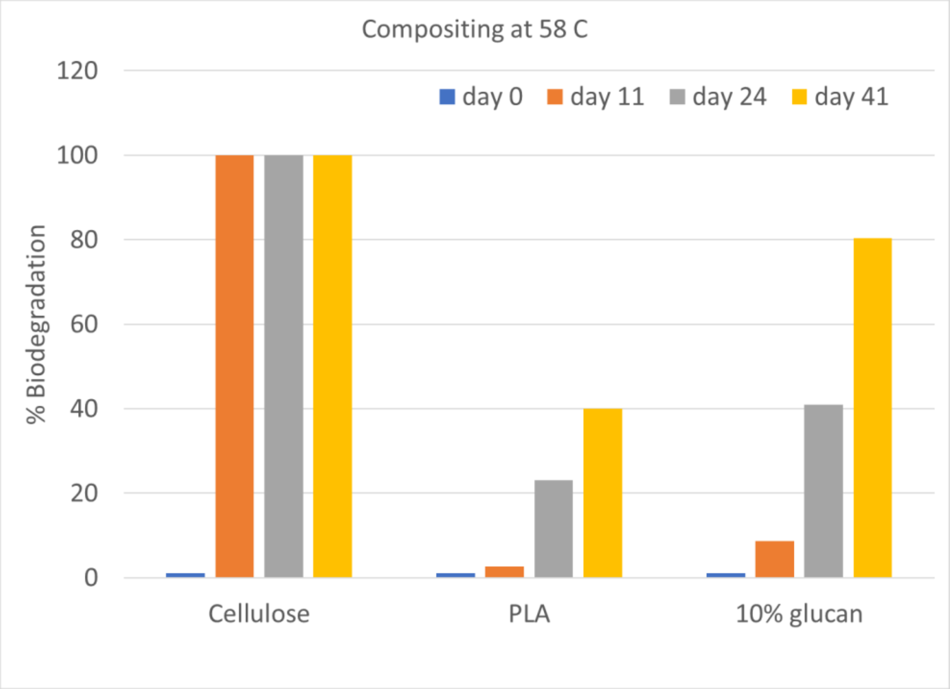
Target Injection Molding and Extrusion Grades

Assessment of Coupling Additives to Improve Thermal Stability

Poly-Saccharide %	Coupling Additive	Yield stress (Mpa)	Notched Izod (J/M)	Elongation %	HDT (C)	Biocontent
0	-	50	27	<5	55-100	100%
20	-	55	35	5 - 8	67	100%
20	A	52	32	5	130	98%
30	A	48	32	5	130	98%
20	B	45	27	4.5	140	96%
20	C	45	41	15	140	90%

PLA / POLYSACCHARIDE COMPOUNDS: BIODEGRADABILITY SYNERGIES

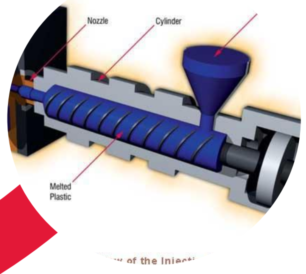
- PolySaccharides Meet fundamental Biodegradability Requirements across key certification categories
- PLA/PolySaccharide Compounds with Synergistic Effect



Engineered PolySaccharides in biobased thermoplastics

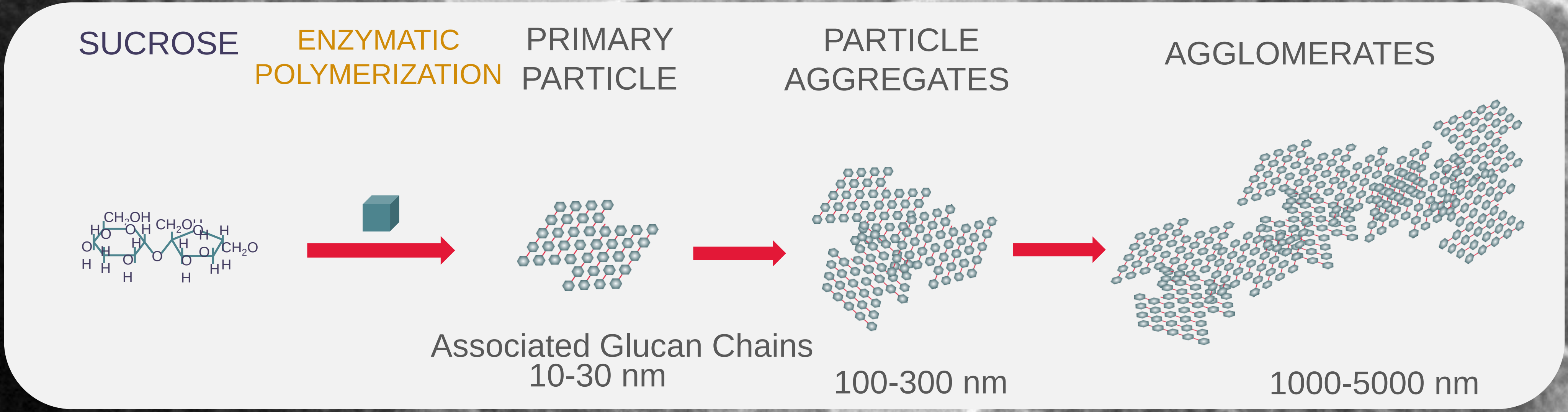
Meeting biodegradability targets at high bio content

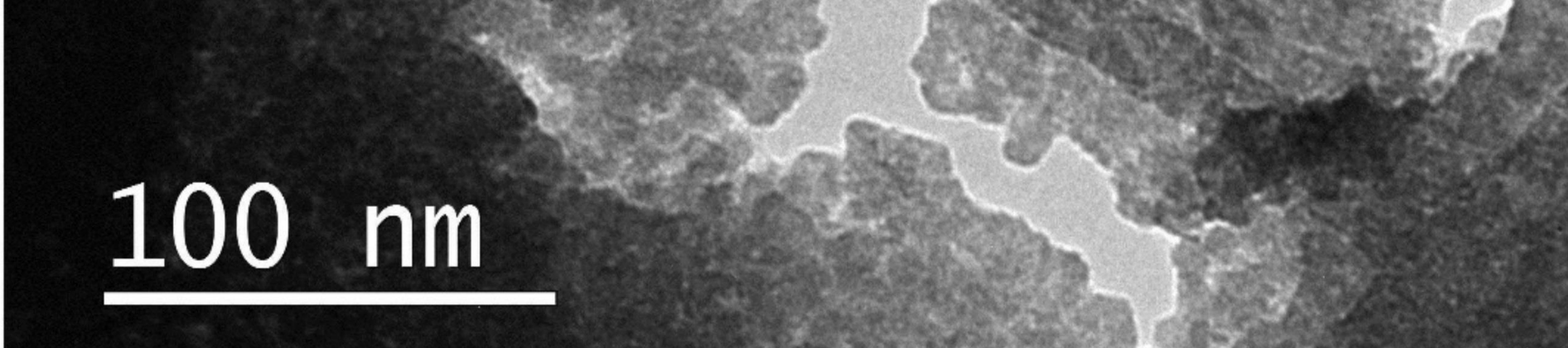
Improved performance
Modulus, HDT, Color



Processability
injection cycle time & throughput

BIOPROCESS CONTROL:
FROM MOLECULAR DESIGN TO POLYMER ARCHITECTURE & PARTICLE MORPHOLOGY



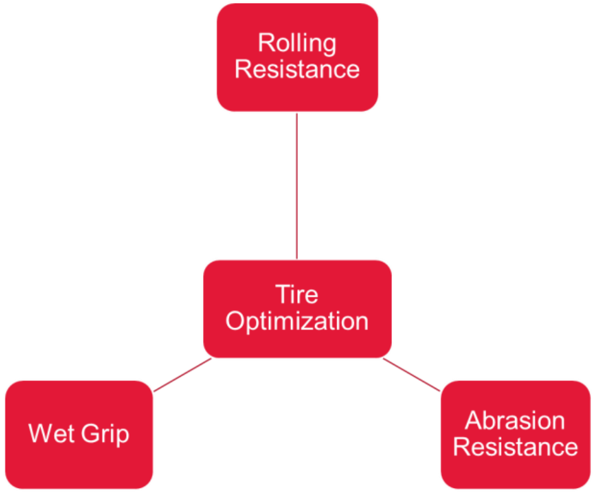


TEM Images of Glucan polymer from Enzymatic Polymerization BioProcess: Primary Particle

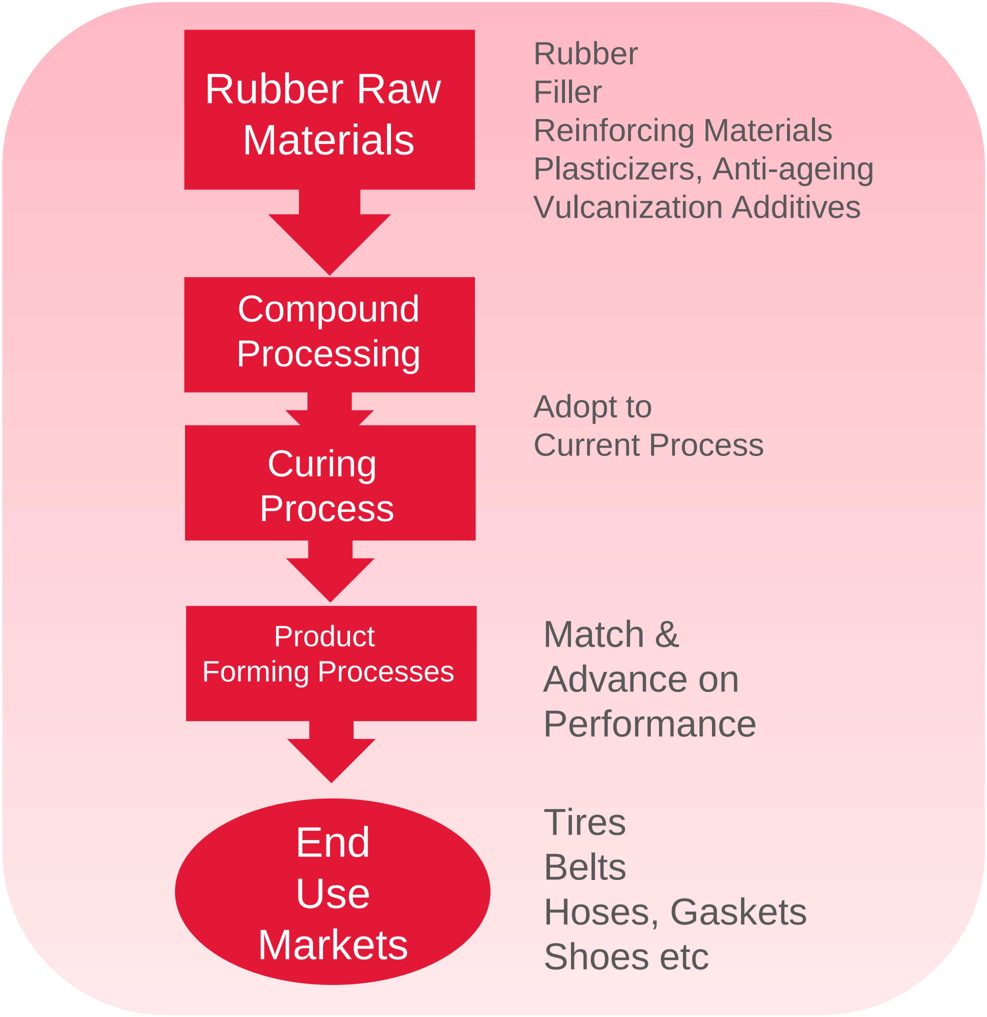
NUVOLVE™ ENGINEERED POLYSACCHARIDES: REINFORCING FILLER APPLICATION OPPORTUNITIES

Key Requirements:

- Compatibility with Rubber Formulations
- Maintain or Improve Properties
- Advancing Sustainability & Performance

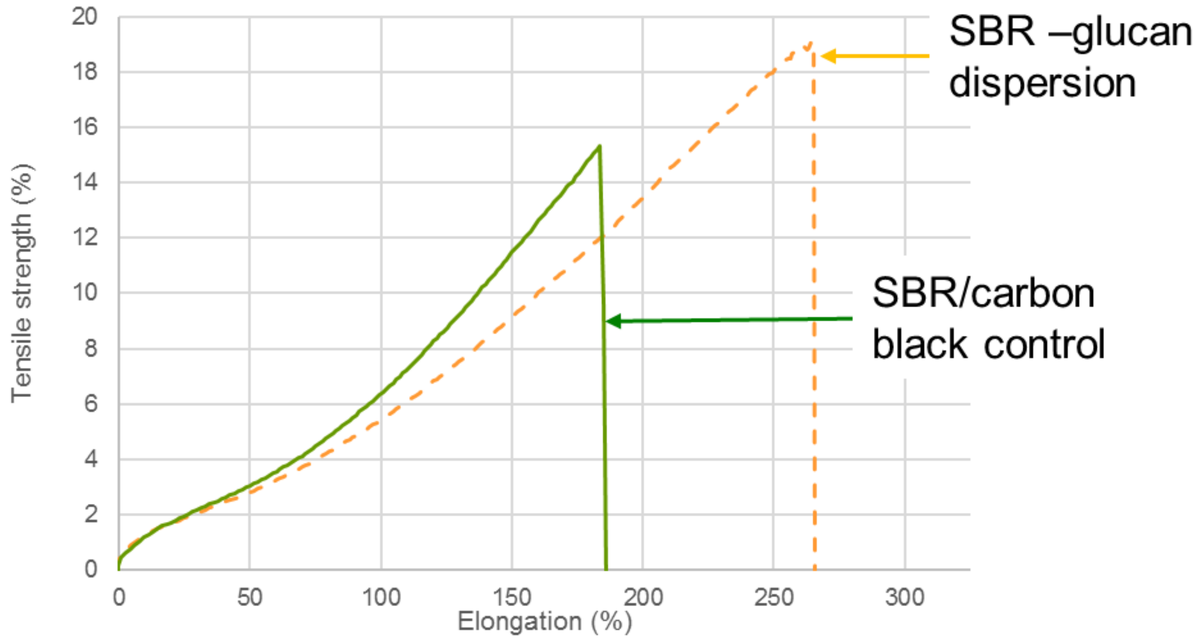


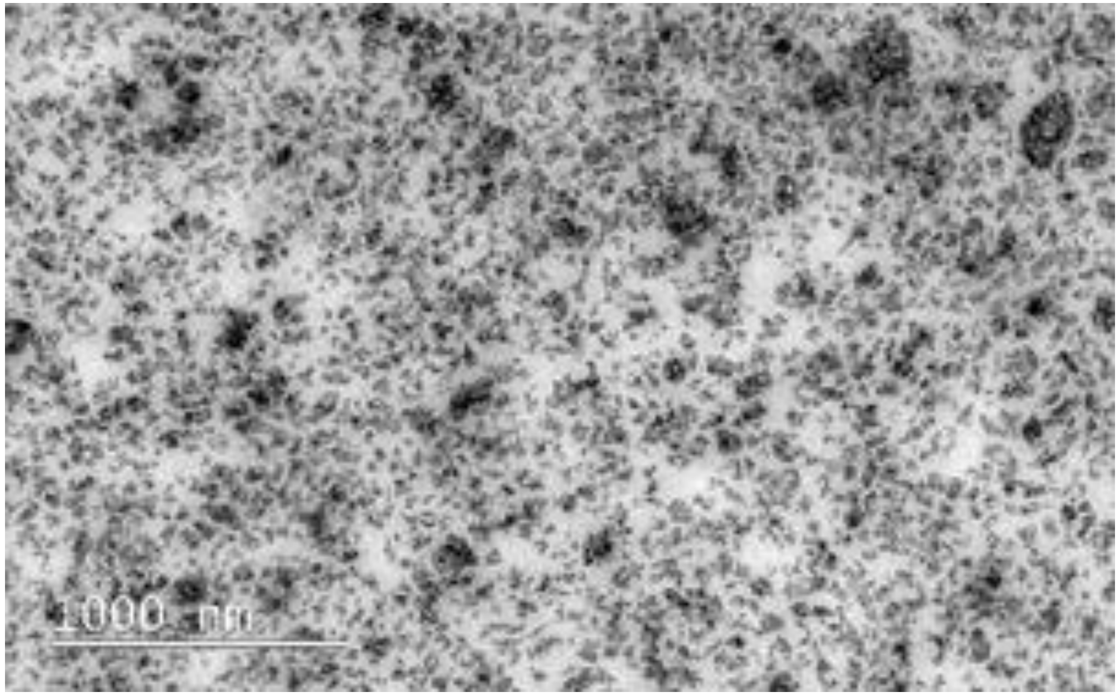
- Rubber/Filler Processing
- Base Line Composites Results
- Examples: Carbon Black & Silica Replacement



ASSESSMENT IN TYPICAL RUBBER PROCESSING: COMPOUND DEVELOPMENT

- Replace carbon black and/or silicas at various levels
- Current coupling agents viable
- Good wetting, homogenous, non-porous
- Lower torque – Decrease in viscosity



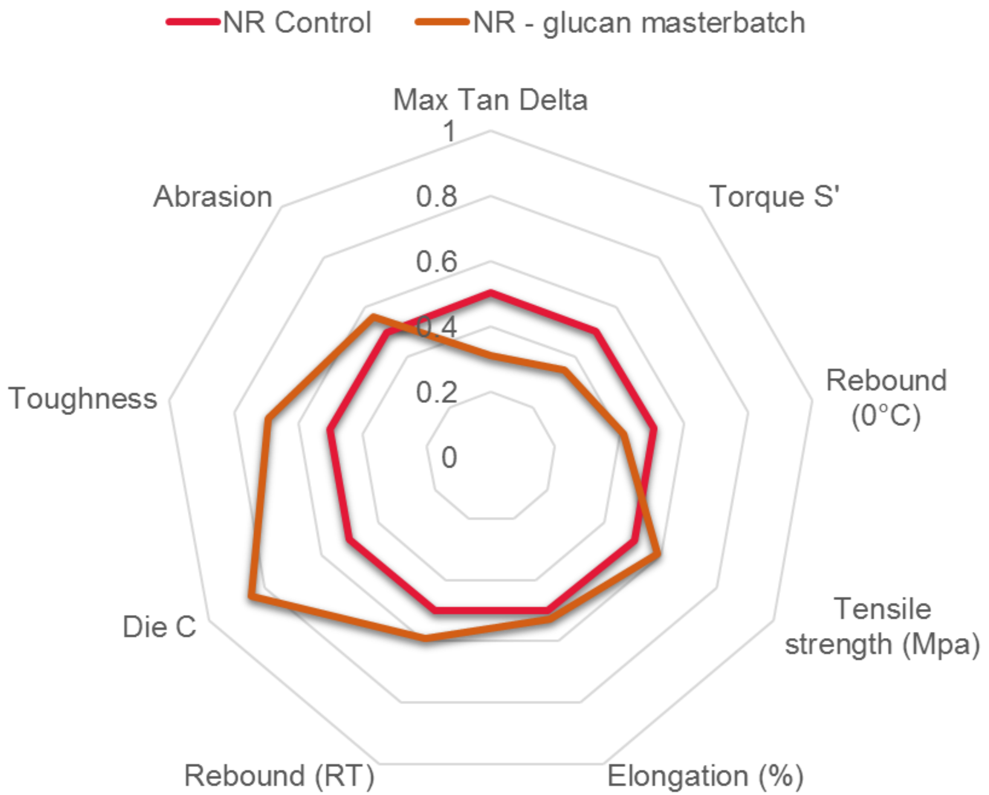


TEM images displays the dispersion polysaccharide – silica hybrid reinforcing fillers in rubber compounds

- Effective dispersion in rubber composite
- No significant agglomeration of polysaccharide particles observed

EXAMPLE: CARBON BLACK REPLACEMENT IN TIRE TREAD FORMULATIONS

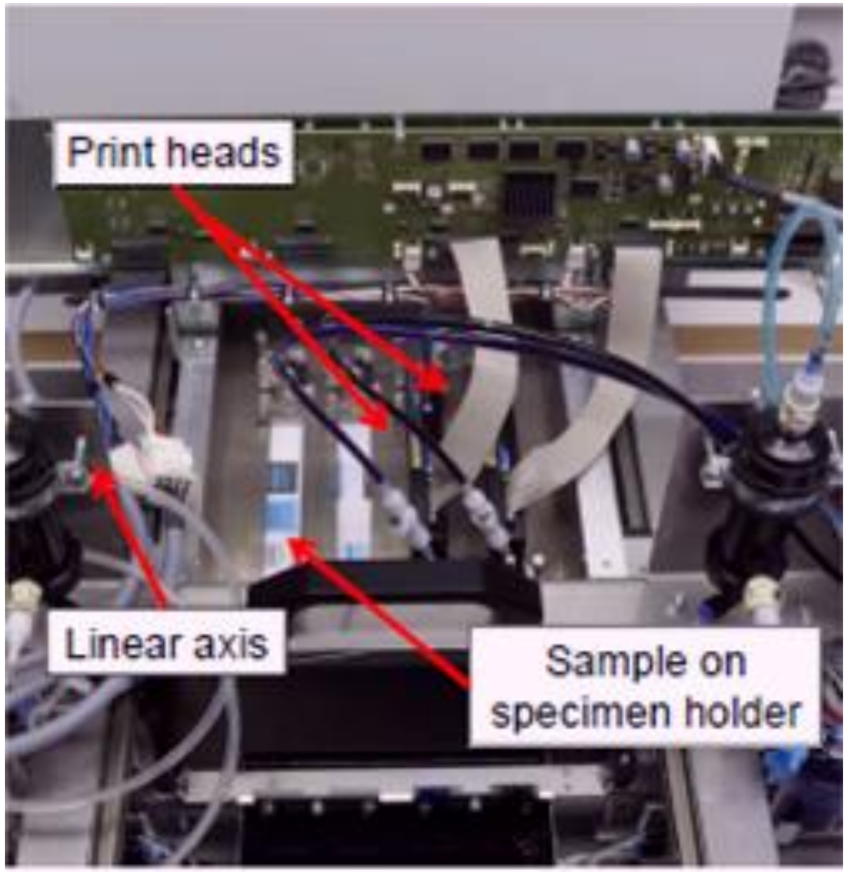
- Improvement of elongation & overall toughness
- Tan delta (60C) of composites has improved
- Rebound: increased at RT & decreased at 0°C
- Lower density – 10-20%



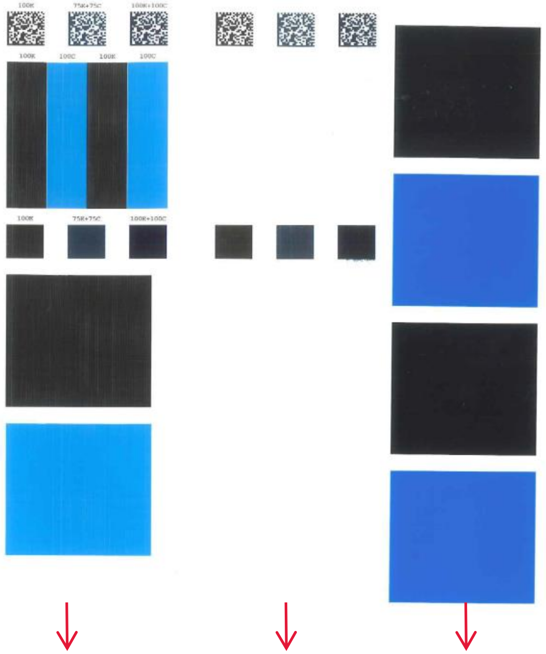
- Different grades of polysaccharide fillers
  - Surface area change
  - Lower particle size / higher surface activity
  - Improve abrasion / maintain Tan delta (60C)

Compound Compatibility & Positive Impact on Dynamic Performance

PTS MUNICH LAB-HIGH SPEED INKJET – PRINTER TEST UNIT



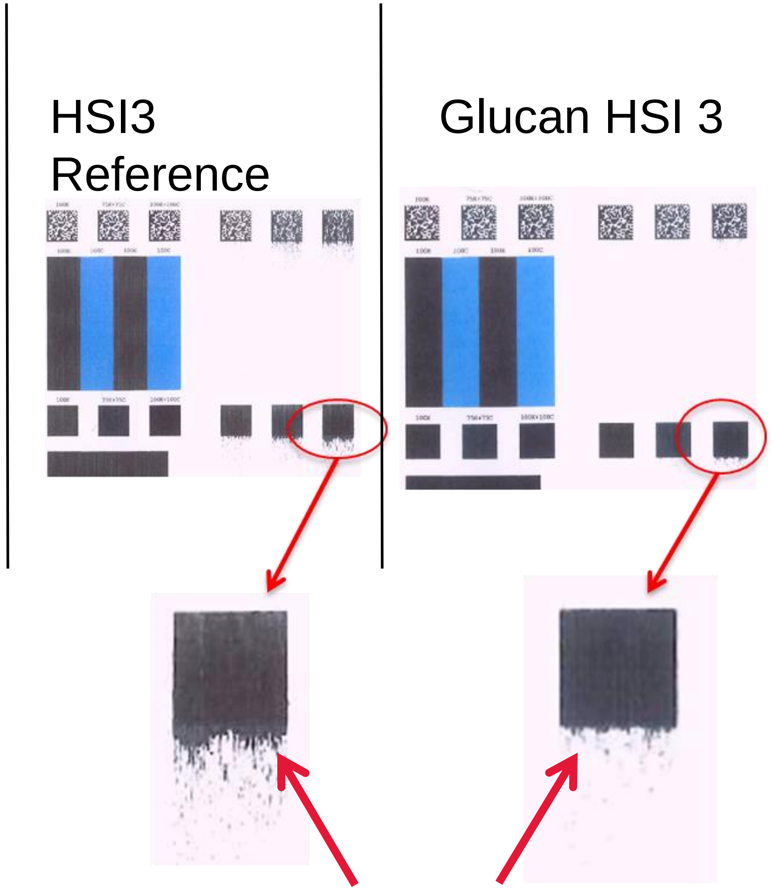
- The printing system is equipped with two Industrial Oce/Canon print heads (piezo), and a wipe unit
- Inks: pigment ink Oce black and cyan
- Printing speed: up to 100 m/min
- Wiping of 3 Data Matrix Codes after predefined drying time 1,7 seconds



HSI Not wiped | HSI Wiped (1,7 s) | Desk Jet

GLUCAN CAN MAKE A SIMPLE COATED PAPER INK JET PRINTABLE

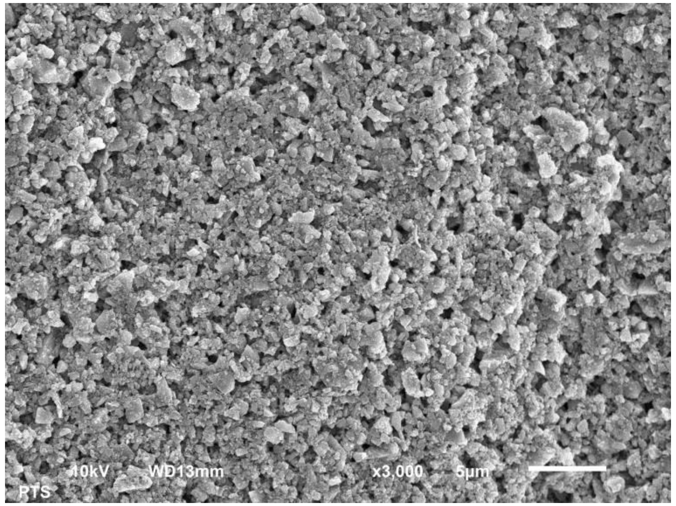
parameters		Control S4-HSI3	S4-HSI3.1
Coating Formulations		UF CaCO3 – 100 Starch - 15	UF CaCO3 – 70 Starch – 15 Glucan - 30
coating weight	g/m²	8,1	8,3
coating thickness	µm	5,4	7
printing test with HSI printer			
wipe-test after 1,7 sec	600 dpi	A/F	A/A
non wiped/wiped	900 dpi	A/-	A/C
	1200 dpi	A/-	B/F
Printing Test with Desk Top Printer			
Color Density Power Spectrum Black/ Cyan		22.6 90	25.8 93.2
Mottle Index Power Spectrum Black/Cyan		10.3 32.7	9.8 15



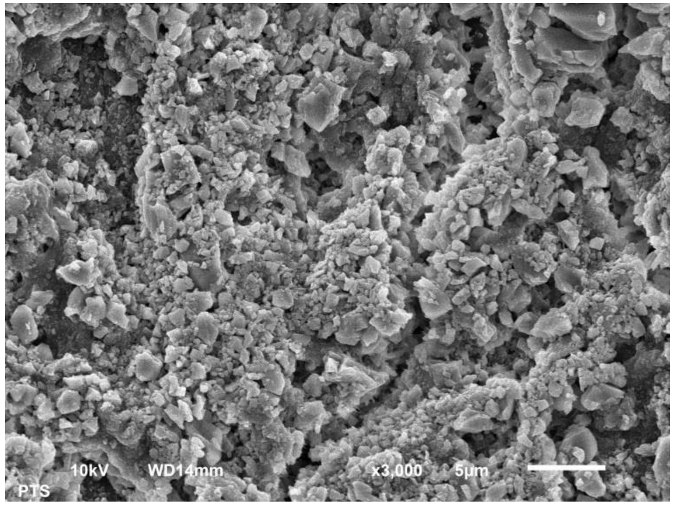
Less „smear“ due to faster ink absorption. Better color density, dot gain and mottle index.

HIGH SPEED INKJET – SEM HSI 3 (X 3000)

Polysaccharide Increases Porosity of Coating Enhancing Water Absorption



HSI 3 *100 parts UF CaCO3*

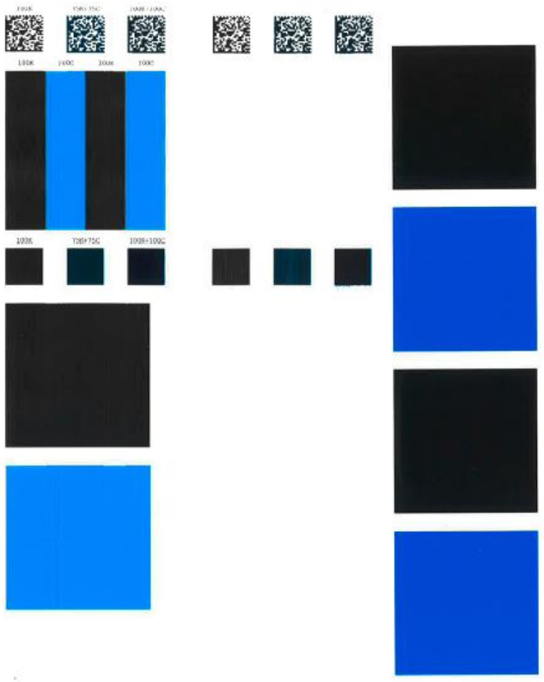


HSI 3.1 *30 parts PSCC, 70 parts UF CaCO3*

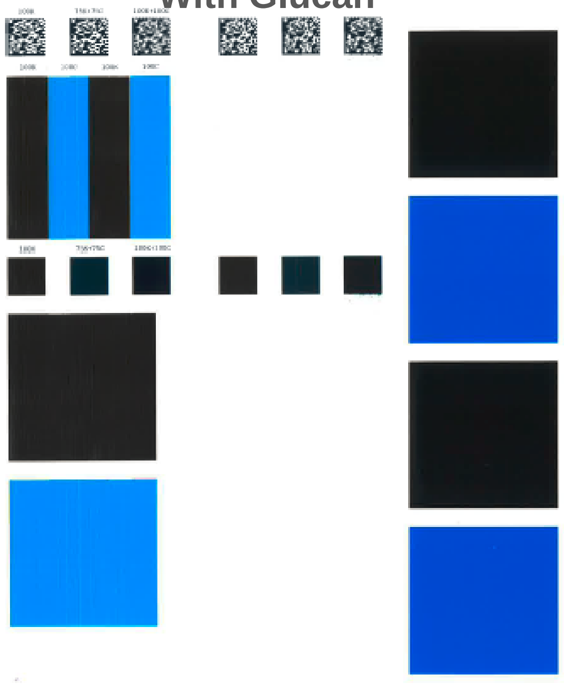
NO LOSS IN QUALITY - REDUCTION IN SILICA AND BINDERS IN HIGH QUALITY IJ COATING

parameters		Control	S1-HSI1.4
Coating Formulations		Silica 1 – 75 Silica 2 - 18 -------------- PVOH – 34 PVAc – 50 Others - 17	Silica 1 – 50 Silica 2 – 18 Glucan – 25 ----------------- PVOH – 34 PVAc – 40 Others -17
coating weight	g/m²	6.1	6.2
coating thickness	µm	18.3	19.1
printing test with HSI printer			
wipe-test after 1,7 sec	600 dpi	A/A	A/A
non wiped/wiped	900 dpi	A/A	A/A
	1200 dpi	A/F	A/F
Printing Test with Desk Top Printer			
Color Density Power Spectrum Black/ Cyan		34.5 90	35.1 92.3
Mottle Index Power Spectrum Black/Cyan		0.6 1.2	0.8 1.9

Control



Replace 25 parts Si With Glucan



NUVOLVE™ ENGINEERED POLYSACCHARIDES THROUGH ENZYMATIC POLYMERIZATION

INNOVATIVE SCIENCE ↓ HIGH PERFORMANCE	SCALABLE SUPPLY ↓ ACCESSIBLE & AFFORDABLE	RENEWABLE SOURCING ↓ RESPONSIBLE BIOMATERIALS
New Class of Renewable Material with Unique Properties	Advancing to Commercial Reality	Rapidly Renewable, Regional Feedstock
Key Processing Benefits	Multi ton quantities available for Development	LCA, Land Use, Light Weighing & Reduced Fuel Consumption

THANK YOU FOR YOUR ATTENTION

Learn more about DuPont Biomaterials

biosciences.dupont.com/biomaterials

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