Chemistry And Technology Information Series 2021

Development of Accelerator-Free and Sustainable Technology For Nitrile Gloves

Dr. Zhenli Wei 12th Oct. 2021

Preface
– Objectives of the Presentation

This presentation follows Dr. Eng Aik Hwee's earlier presentation in Jan. 2021 with the title of "**Research Opportunities in Rubber Glove Industry in Malaysia**" and shares the same objectives as Dr. Eng stated in his presentation:

Malaysia is the world's largest exporter of rubber gloves, with a market share of about 67% in 2020 valued at RM32billion. It is an important export revenue. However, the research interest among the local researchers are not high.

Therefore, the objectives of this presentation are:

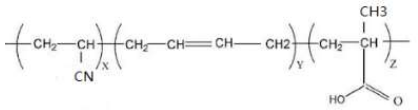
- To encourage more rubber glove research among the local researchers
- To provide some specific ideas on the areas of research with examples

My presentation today focuses on the NBR glove's raw material – XNBR latex, and shows how the development of new chemistries in this polymer field can help for the sustainability of the glove industrial and for glove end users.

(Some data and photos downloaded from internet and used for education purpose only)

Malaysia is the World's #1 Rubber Glove Producing Nation

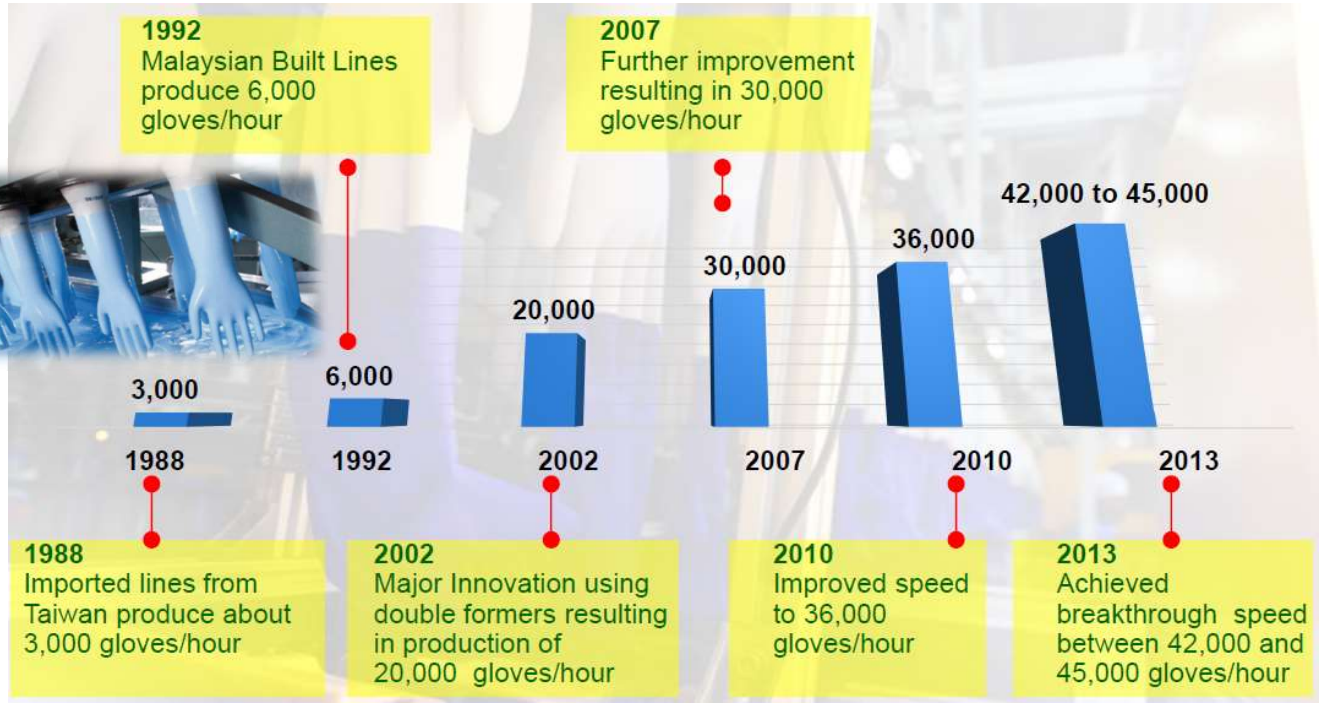
Carboxylated Nitrile Butadiene Rubber (XNBR):

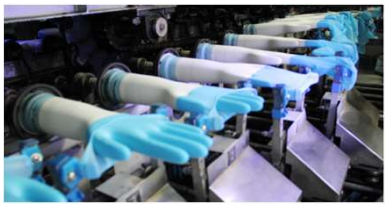


Preface
– Background for Rubber Glove Industry

- **Rubber gloves are made by the latex dipping process**
- **Modernization and automation led to quantum leaps in glove productivity and yield**
- **Further improvements need the joint efforts of NBR latex scientists and process engineers, as well as fundamental studies with researchers at universities**

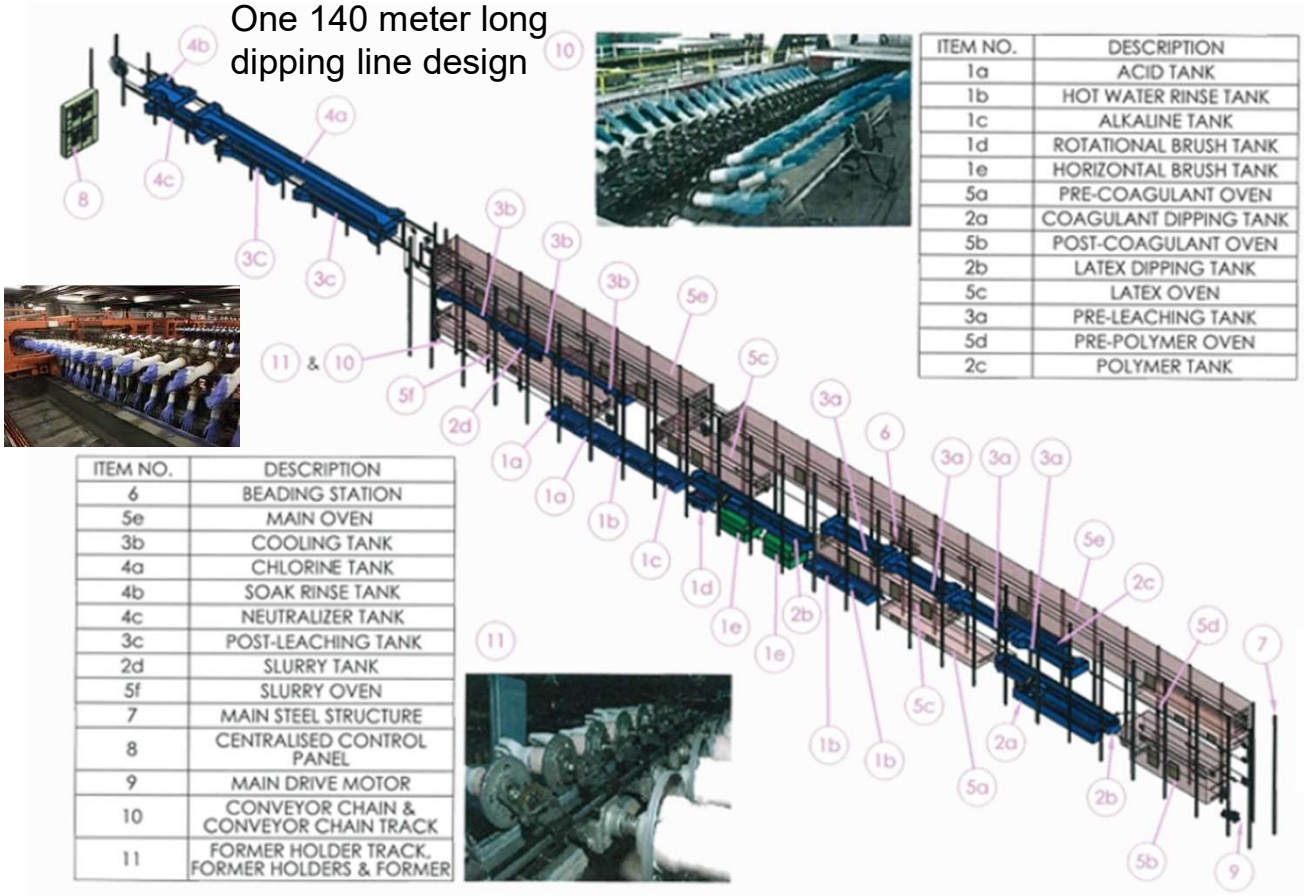
Data from Malaysia Rubber Glove Manufacturers Association (MARGMA)





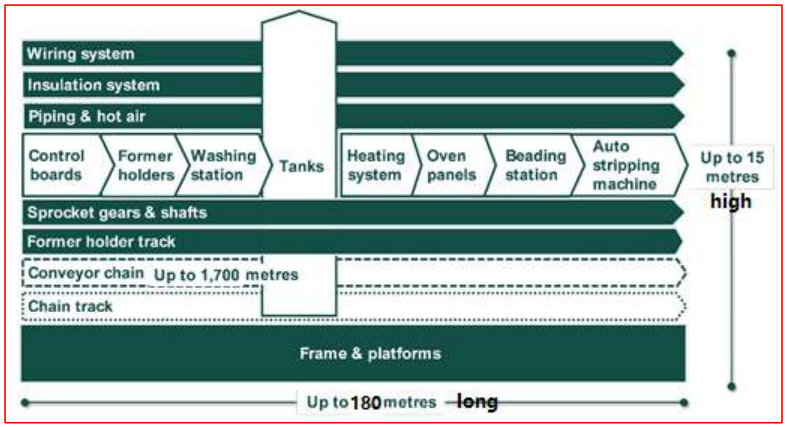
Preface
– Background for Rubber Glove Industry

One 140 meter long dipping line design



ITEM NO.	DESCRIPTION
1a	ACID TANK
1b	HOT WATER RINSE TANK
1c	ALKALINE TANK
1d	ROTATIONAL BRUSH TANK
1e	HORIZONTAL BRUSH TANK
5a	PRE-COAGULANT OVEN
2a	COAGULANT DIPPING TANK
5b	POST-COAGULANT OVEN
2b	LATEX DIPPING TANK
5c	LATEX OVEN
3a	PRE-LEACHING TANK
5d	PRE-POLYMER OVEN
2c	POLYMER TANK

ITEM NO.	DESCRIPTION
6	BEADING STATION
5e	MAIN OVEN
3b	COOLING TANK
4a	CHLORINE TANK
4b	SOAK RINSE TANK
4c	NEUTRALIZER TANK
3c	POST-LEACHING TANK
2d	SLURRY TANK
5f	SLURRY OVEN
7	MAIN STEEL STRUCTURE
8	CENTRALISED CONTROL PANEL
9	MAIN DRIVE MOTOR
10	CONVEYOR CHAIN & CONVEYOR CHAIN TRACK
11	FORMER HOLDER TRACK, FORMER HOLDERS & FORMER



A modern glove dipping line can be up to 180m long and 5 stories high with more than 34,000 heavy ceramic formers loaded onto metal conveyor chains running along the line

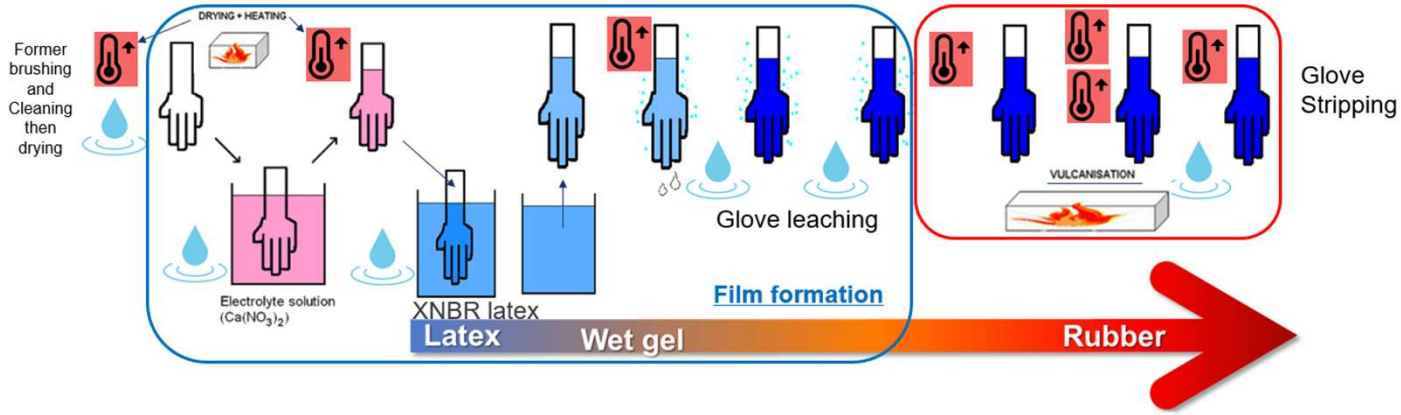
A sizable modern glove dipping plant now can cost US$ > 40M Capex

Data from Malaysia Rubber Glove Manufacturers Association (MARGMA) and from internet for educational purposes

synthomer

Preface
– Background for Rubber Glove Industry

- **Faster dipping line speed and reducing glove weight (thinner gloves with lower glove weight per piece) keep pushing XNBR latex suppliers for innovations related to the raw polymer material**



Data from Malaysia Rubber Glove Manufacturers Association (MARGMA)

Outline

- **Overview of Synthomer and our nitrile latex**
- **Motivation for accelerator-free crosslinking systems for NBR gloves**
  - Challenges related to normal crosslinking using sulphur and accelerators
- **Overview of accelerator-free crosslinking systems for nitrile latex**

SYNOVUS™

- Benefits of Synthomer's **SyNovus** Technology with low curing temperature
- Better Life Cycle Assessment (LCA) for gloves

SYNOVUS™ PLUS

- Synthomer's new technology platform towards **glove circular economy**
  - Better physical performance for **even lower carbon footprint**
  - Better sustainability achievable by **better end-of-life management**
- **Summary**

A Growing Supplier of Specialty Polymers

A leading global supplier of water-based and specialty polymers with **revenues of £1.65bn** and **EBITDA £259.4m**; Headquarter in London (UK)

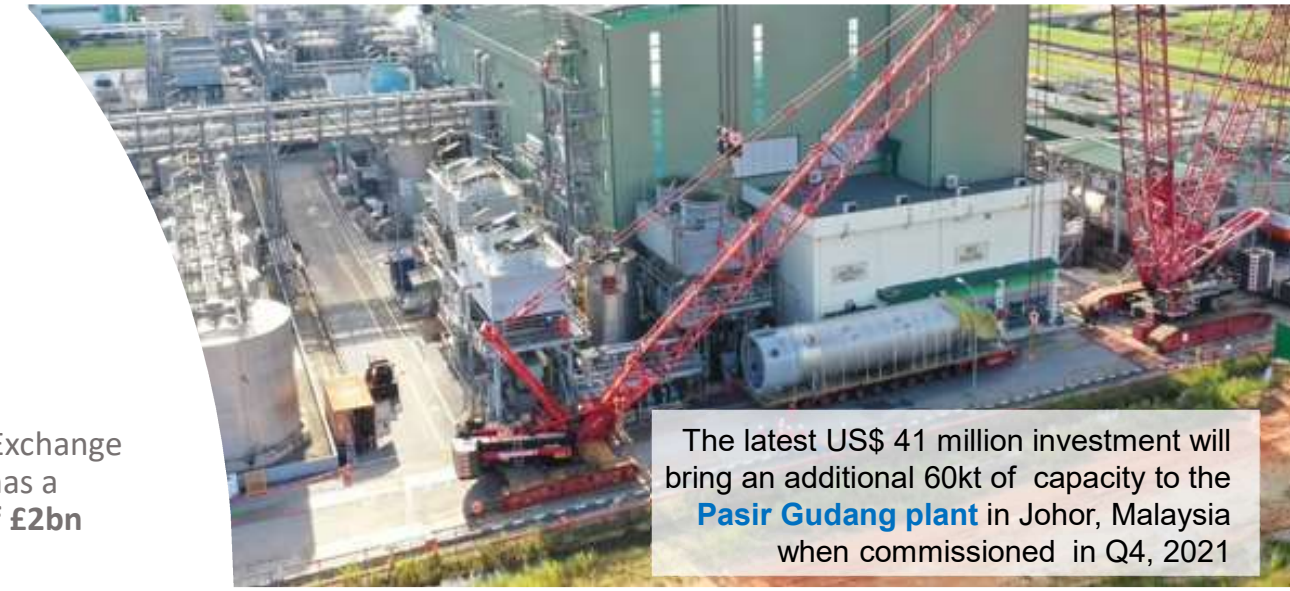
FTSE 250

Listed on London Stock Exchange since 1971; Synthomer has a **Market Capitalization of £2bn**

A **strong track record** of organic growth and M&A

No. 2 global supplier of Nitrile Butadiene Rubber Latex in terms of volume with **two NBR plants in Malaysia** and **one plant in Italy**

ca. **4,750 employees** around the world in 18 countries working in **37 manufacturing sites** and **4 Innovation Centres** in Europe, North America and Asia



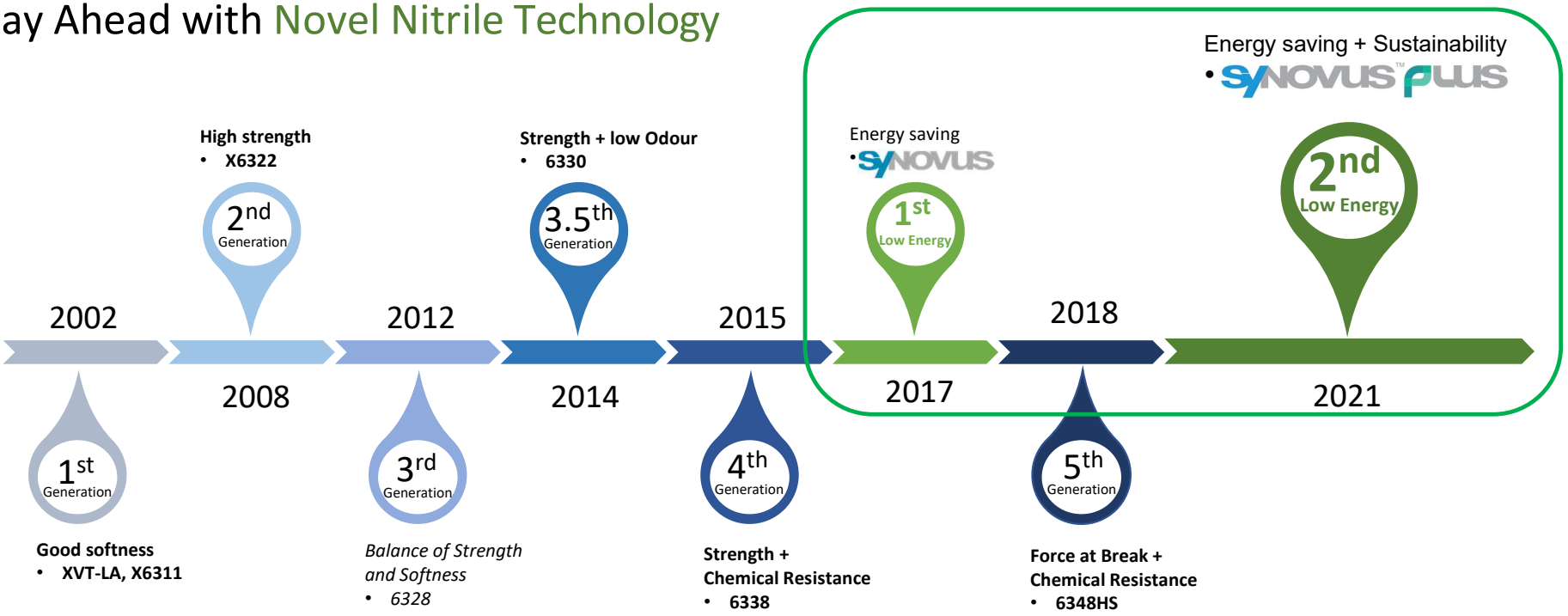
The latest US$ 41 million investment will bring an additional 60kt of capacity to the **Pasir Gudang plant** in Johor, Malaysia when commissioned in Q4, 2021

US$ 9 million investment for the new **Asia Innovation Centre** in Johor, Malaysia which opened in Nov. 2020

Synthomer Nitrile Latex Evolution

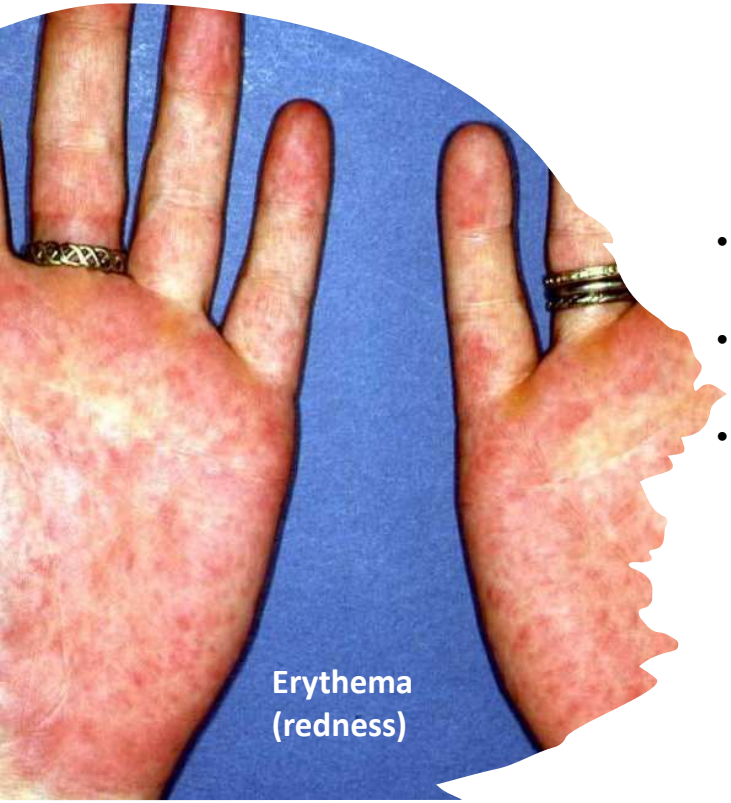
Synthomer offers a wide range of NBR latex grades which meets different glove application needs and is committed to

Stay Ahead with Novel Nitrile Technology

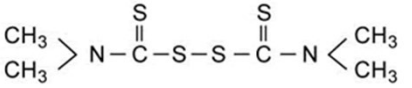


Motivations for Accelerator-Free Gloves:

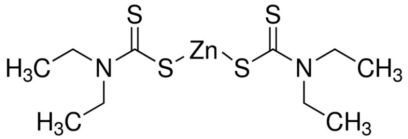
Type IV allergy caused by accelerators used in sulfur crosslinking



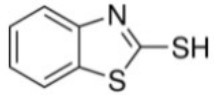
- Accelerators caused 82% of reported gloves-associated allergic contact dermatitis (ACD) or type IV chemical allergy
- These accelerators include thiurams, dithiocarbamates, and mercaptobenzothiazole[1]
- The residues from these accelerators have become a major concern because of their ability to sensitize users and elicit chemical allergic reactions[2,3]. Therefore, **accelerator-free technology has been the growing choice for the glove industry and needed by end users**



Tetra Methyl Thiuram Disulphide (TMTD)



Zinc diethyldithiocarbamate (ZDEC)



2-mercaptobenzothiazole

1. *Isaksson M. Dental materials. In: Johansen JD, Frosch PJ, Lepoittevin J-P (eds). Contact dermatitis. Berlin, Heidelberg: Springer Berlin Heidelberg, 2011: 763–91.*
2. *Heese A, Hintzenstern JV, Peters K, Koch HU, Hornstein OP. 1991. Allergic and irritant reactions to rubber gloves in medical health services. Journal of the American Academy of Dermatology. 25:831-839.*
3. *Gardner N. 2008 Oct. Shield Scientific: health and safety international.*

Normal Crosslinking with Sulfur and Accelerators for NBR Gloves

Typical XNBR latex, compounding recipe and dipping process information

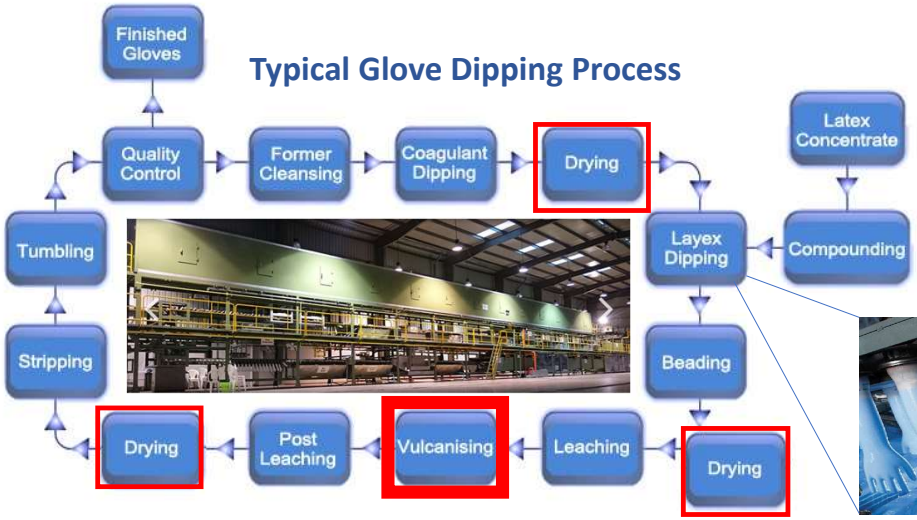
NBR latex Composition	
Acrylonitrile	25~35 phr
Butadiene	60~70 phr
Carboxylic acid	4~6 phr
Surfactant SDBS etc.	
Total solid content	45 wt%

Compounding Ingredient	
Zinc oxide, ZnO	1.0~1.2 phr
Sulfur	~0.8 phr
Accelerator (ZDEC*)	~0.7 phr
Titanium dioxide, TiO_2	~1.0 phr
Pigments	As needed
pH	9.5-10.5
Total solid content	20% or below

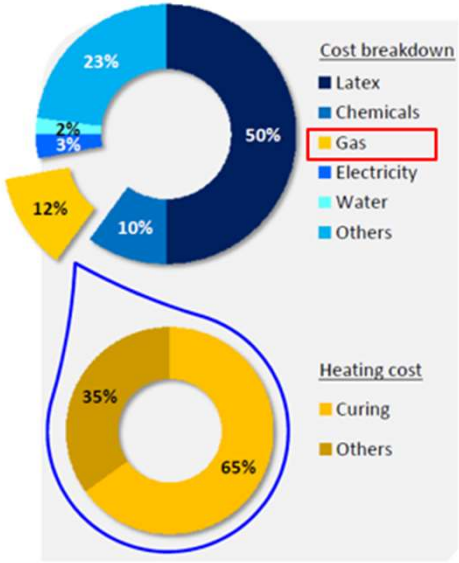
Data from Malaysia Rubber Glove Manufacturers Association (MARGMA) and from internet

Typical dipping process conditions

- 24 hours maturation after compounding
- Coagulant solution at 18 wt%
- Single or double dipping
- 5 sec dwell time
- Drying @100 ^{0}C for 1 min
- **Curing at ~ 120 ^{0}C** for 10~20 min



Glove Manufacturing Cost Breakdown



Overview of Accelerator-Free Technologies for NBR Gloves

Chemistries reported in different patent applications:

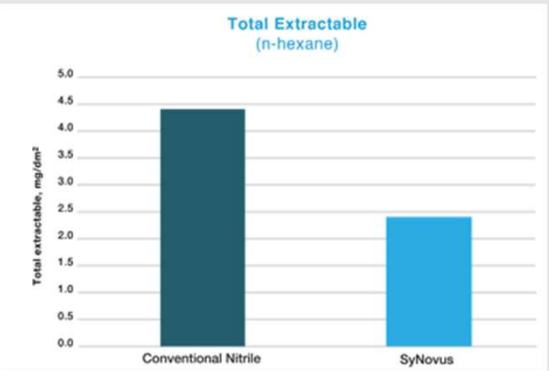
- Polyoxazoline
- Diacetone acrylamide dihydrazide
- 2-acetoxyethyl methacrylate/dihydrazide
- Triethylenetetramine
- Phenolic methylol compound
- Reactive aqueous urethane compound
- Modified polyamide
- Polyallylamine
- Acrylamine polymer
- Ethyleneimine
- Triethanolamine
- Aziridine compound
- Water-soluble methylol melamine compound
- Silane coupling agent
- **Aluminum ion derivatives crosslink systems**
- **Polycarbodiimide**
- **Aqueous epoxy compound**

US8044138
WO2010035955
WO2011068394
WO2012043894
WO2012043893
WO2014034889
WO2015129871
WO2015142155
JP6646949
WO2016013666
WO2016072835
WO2017116227
WO2017126660
WO2017217542

WO2017006385
US2017099889
US20180016409
WO2018048122
WO2019172539
US20190119465
WO2019156550
WO2019194056
WO2020195712
WO202110343
WO202110334

Benefits of SyNovus Technology
-- Accelerator-Free & Low Temperature Curing

- Technology based on novel polymer designed for accelerator-free crosslinking
- Allows glove producers to **significantly reduce the glove curing temperature and decrease overall energy usage by > 20%**
- The technology also helps **increase manufacturing efficiency** and **lower production cost** by using lesser raw materials without compromising on barrier protection.



Accelerator free

Technology based on novel polymer design for accelerator-free gloves which **prevent allergies for end user**

This feature strongly appeals to glove manufacturers and end users

NO COMPROMISE ON BARRIER PROTECTION

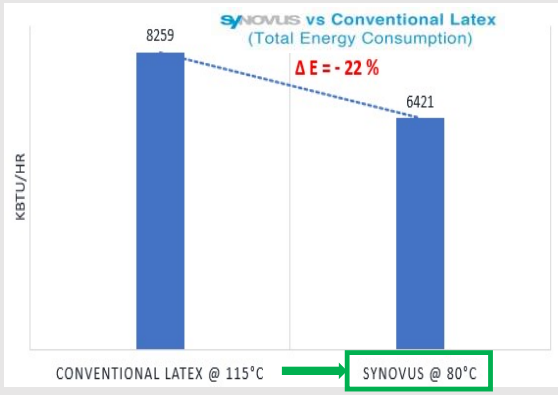
- **Tensile strength**
- **High durability**
- **Chemical resistance**

BETTER OPERATION EFFICIENCY

- **No maturation needed**
- **Lower processing cost**
- **Minimise compounding complication**

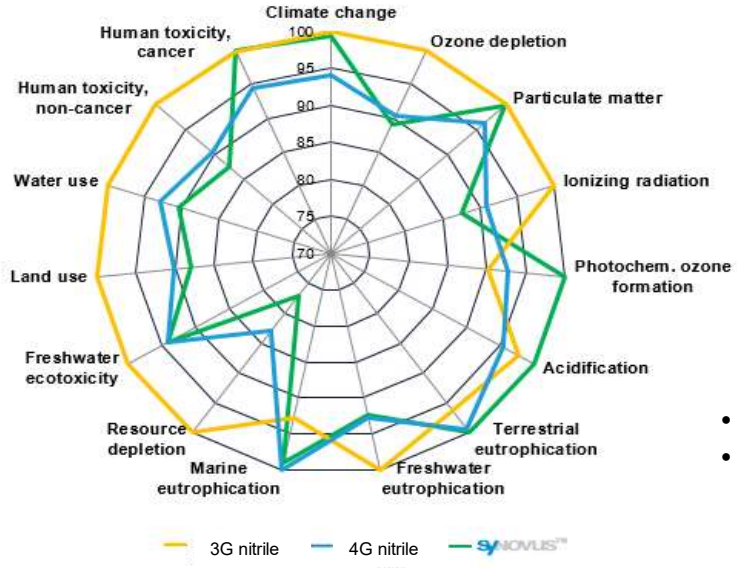
SYNOVUS™

Significantly reduce the glove curing temperature and **decrease overall energy usage by > 20%**



Benefits of SyNovus Technology
-- Life Cycle Assessment Reported in 2019 for SyNovus Latex

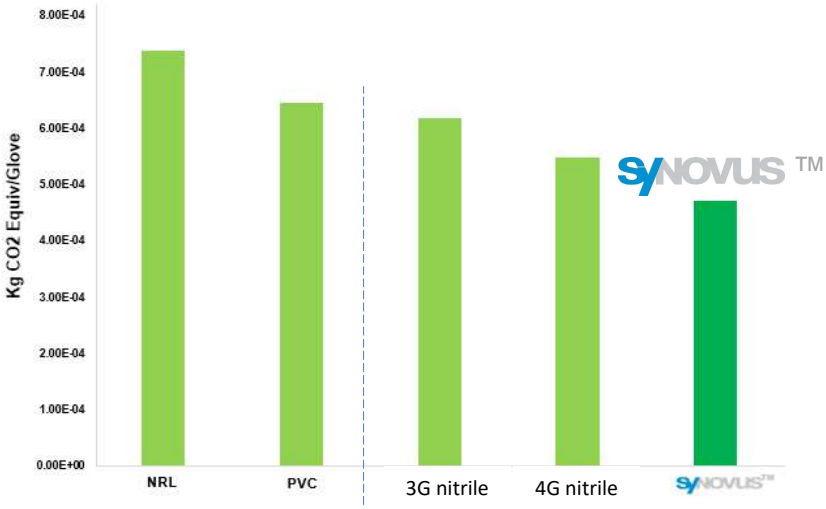
Gloves made by using SyNovus latex demonstrated lowest impact on environment during glove life cycle compared with gloves made by using other conventional NBR latex



Glove made by	Glove weight (g)
SyNovus nitrile	3.3
4G nitrile	**3.3**
3G nitrile	**5.0**
NRL	**5.5**
PVC	**4.0**

- **Lifetime uses: 5 mins**
- **End-of-Life (EoL): Incineration**

Gloves made by using SyNovus latex demonstrated lowest contribution to greenhouse gas during glove life cycle compared with gloves made by using other conventional NBR latex, nature rubber latex (NRL) and Polyvinyl Chloride (PVC) gloves



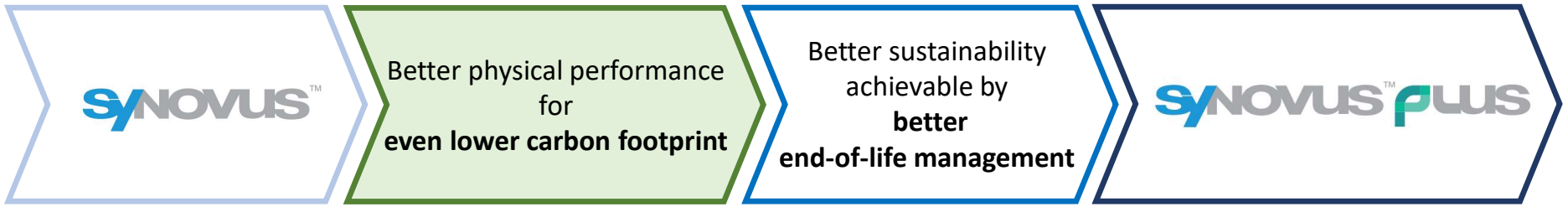
- 15 - 20% lower CO_2 impact than conventional NBR glove technology
- also has an impact up to 30% lower compared to other non-NBR latex technologies

LCA Done By:
Materia Nova

Certified by:
LCIE Bureau Veritas France in accordance to ISO14040, ISO14044 and ISO14071

SyNovus™ Plus Technology Platform towards Glove Circular Economy

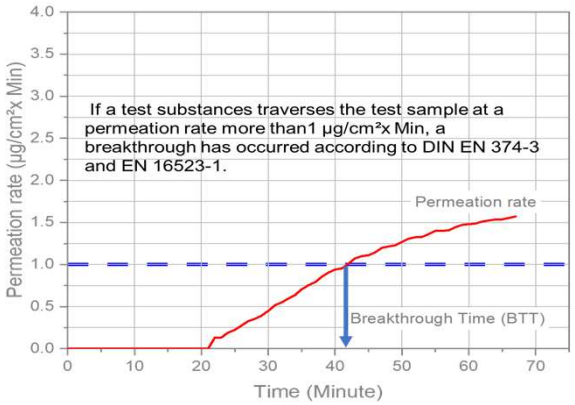
Sustainability is a core part of Synthomer innovation mindset
using a multi-faceted approach for improving human health and reducing environmental impact with a focus on the complete product value chain and cradle-to-grave product life-cycle analysis



Requirements for Medical Gloves

-- while gloves become thinner and thinner

Impermeability test (EN 16523-1)



Durability test

- Unaged gloves with good durability can prevent tearing during stripping the finished gloves off the hand former
- When wearing glove over a period of time, failure of gloves could happen and mostly observed in the crotch between the thumb and forefinger
- Normally > 1 hour (by in-house test method) for unaged gloves

Tensile tests

ASTM D-6319		EN455-2
Unaged	Aged	Unaged & Aged
Tensile: > 14MPa	Tensile: > 14MPa	**Force at Break (FAB)**
EB: > 500%	EB: > 450%	**6 N**
Thickness:	min. 0.05mm	No thickness requirement

ASTM D412 Standard Test Methods for Vulcanized Rubber and Thermoplastic Elastomers - Tension

- Die Cutter: Type C

ASTM D537 Standard Test Method for Rubber – Deterioration in an Air Oven

- Aging Condition:
  100 ± 2 °C, 22 ± 0.3h

SyNovus Plus vs. other latex
-- Compounding Recipe & Process Parameters

Polymer latex

No.	Grade Name	Descriptions
1	Conventional NBR latex	For normal S vulcanization
2	SyNovus latex	SyNovus Generation I
3	SyNovus Plus latex	New Generation SyNovus

Conventional XNBR latex

Carboxylated nitrile latex which requires sulphur and accelerator as vulcanizing agent for rubber crosslink to achieve desired physical properties.

SyNovus Plus latex is a new product with novel technology developed by Synthomer which requires no accelerator or sulphur for the rubber compound with no compromise in barrier properties.

Compounding Recipe

Ingredient	Conventional NBR Latex	SyNovus	SyNovus Plus
ZnO, phr	1.0	1.0	1.0
Sulphur, phr	0.8	–	–
ZDBC, phr	0.7	–	–
TiO2, phr	1.0	1.0	1.0

Typical Dipping Parameters and sample information

Latex pH	: 10.0
	and **9.5 (for SyNovus Plus)**
Latex TSC	: 17%
Former texturing	: Micro-textured
Sample thickness	**: 0.055 – 0.060mm**
Glove weight / size	**: 3.0g / M**
Curing temperature	: **70°C** (& 90°C) for 20 minutes

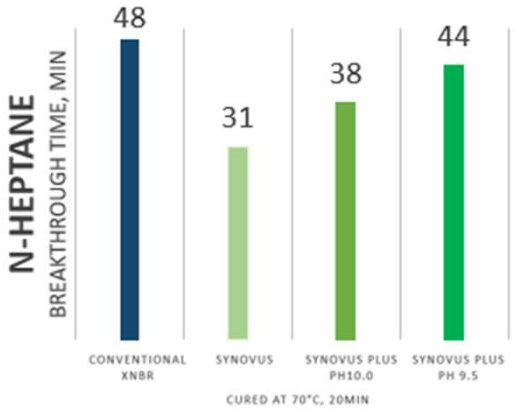
SYNOVUS™ PLUS vs. other latex

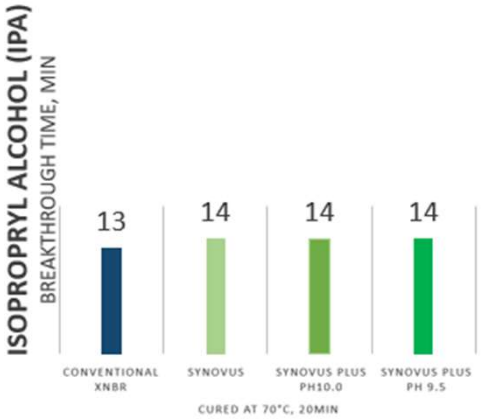
-- Glove performance at 3.0g level

Chemical Resistance

Chemical Resistance

Good chemical resistance performance achieved with suitable compounding pH

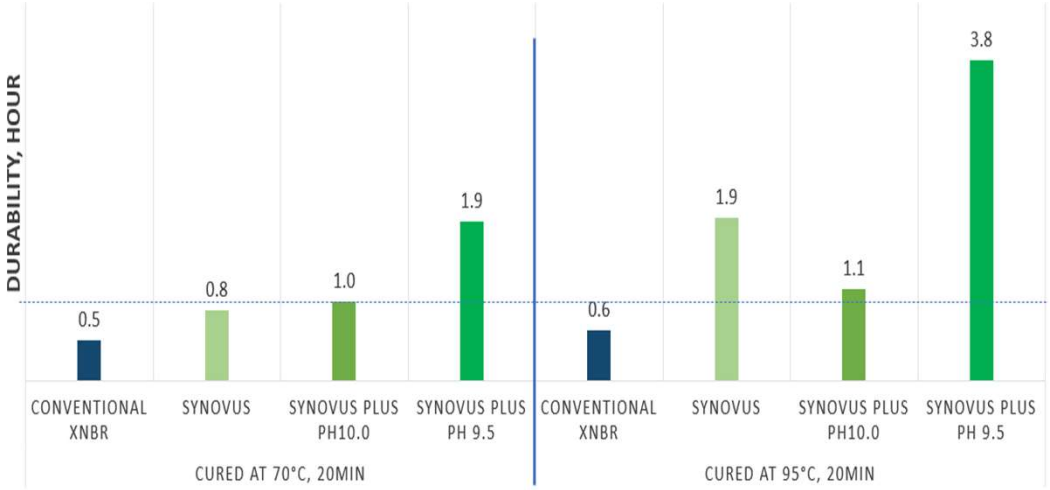




Durability

Durability

SyNovus Plus gloves with good durability can be made by curing at lower T with suitable compounding pH



Remarks:
Thickness (Palm): 0.055-0.060mm

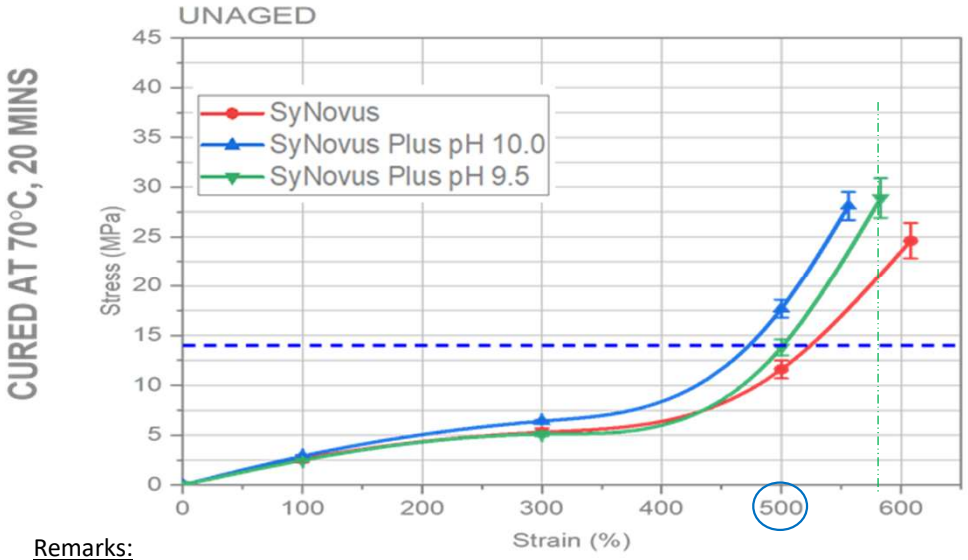
SyNovus Plus vs. other latex
-- Glove performance at 3.0g level

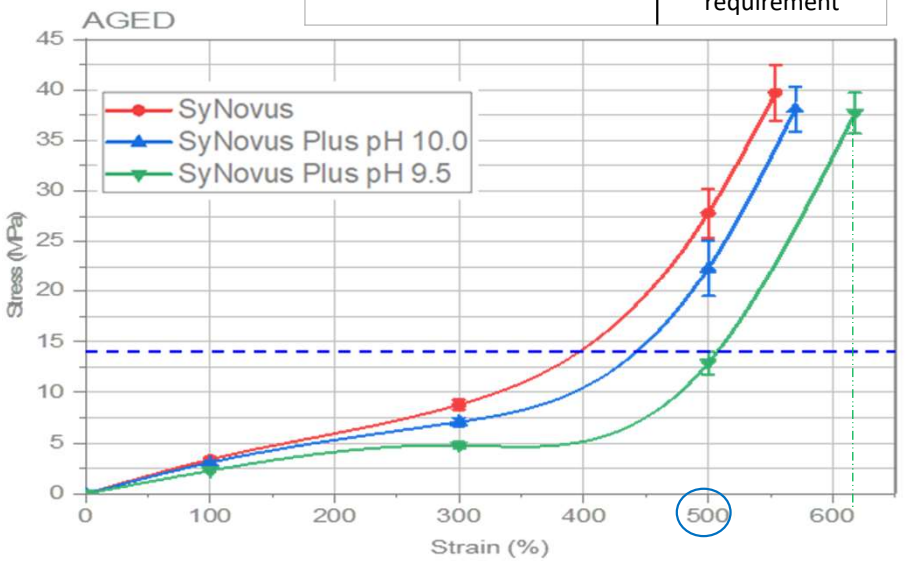
Physical Properties – Tensile & Elongation by ASTM D6319

ASTM D-6319		EN455-2
Unaged	Aged	Unaged & Aged
Tensile: > 14MPa	Tensile: > 14MPa	**Force at Break (FAB)**
EB: > 500%	EB: > 450%	**6 N**
Thickness:	min. 0.05mm	No thickness requirement

Tensile Strength

Gloves with 3.0g or less weight per piece
can be made by using SyNovus Plus latex to **meet ASTM standard with better softness**





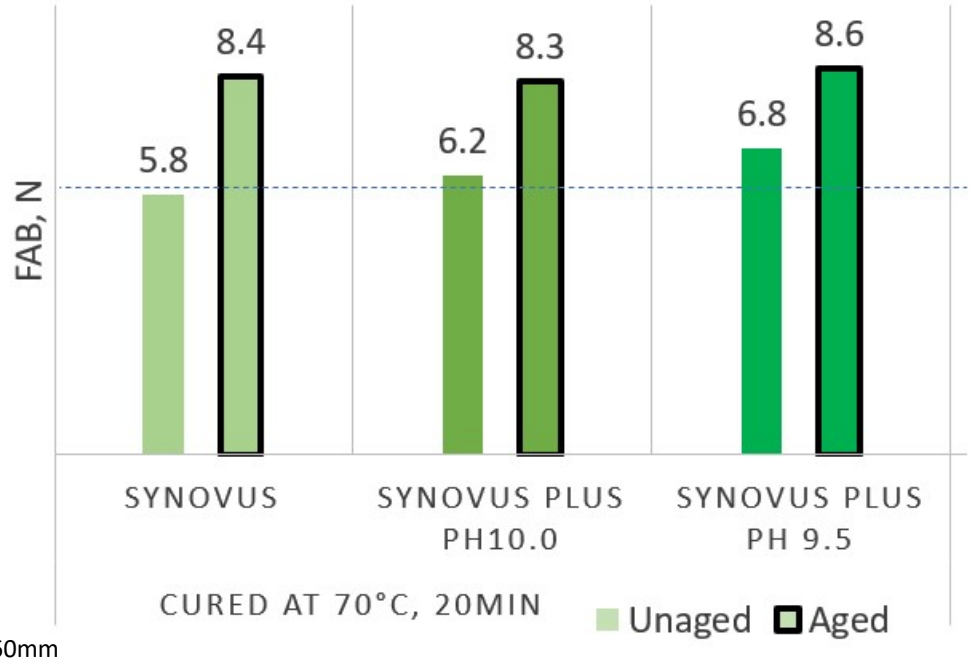
Remarks:
Thickness (Palm): 0.055-0.060mm

SYNOVUS™ PLUS vs. other latex
-- Glove performance at 3.0g level

Physical Properties – Force At Break (FAB) by EN455-2

Tensile Strength

Gloves with 3.0g or less weight per piece can be made by using SyNovus Plus latex to **meet the EN standard**



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EB: > 500%	EB: > 450%	**6 N**
Thickness:	min. 0.05mm	No thickness requirement

(All data presented here is from Synthomer Lab. Real dipping line production trials are on-going)

Remarks:
Thickness (Palm): 0.055-0.060mm

SyNovus™ Plus vs. other latex

SyNovus™ Plus
*PRODUCE **MORE** GLOVES WITH **LESS** RAW MATERIALS*

Regular nitrile latex | SyNovus™ Plus

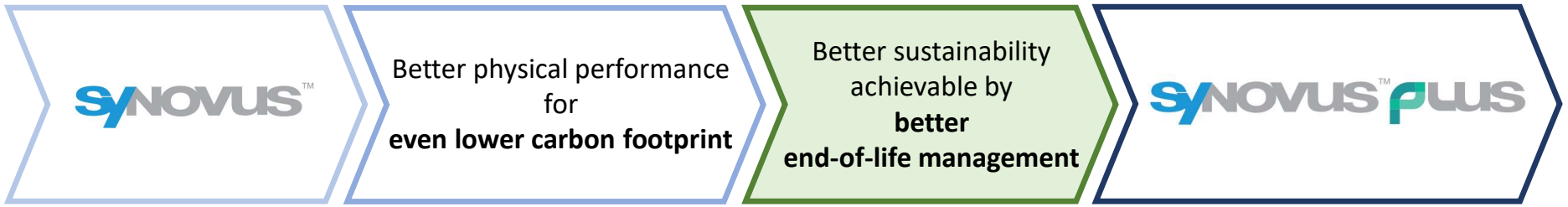
Maximum number of pieces of gloves which can produced from 1 wet ton of NBR latex							
Weight of glove	5g NBR/piece	4.5g NBR/piece	4g NBR/piece	3.5g NBR/piece	3.2g NBR/piece	**3g NBR/piece**	**2.5g NBR/piece**
No. of gloves (pieces)	90,000	100,000	112,500	128,571	140,625	150,000	180,000
% of increase	N/A	11% from 5g gloves	13% from 4.5g gloves	14% from 4g gloves	9% from 3.5g gloves	7% from 3.2g gloves	20% from 3g gloves

Wet ton of NBR latex needed to produce 1 million pieces of gloves							
Weight of glove	5g NBR/piece	4.5g NBR/piece	4g NBR/piece	3.5g NBR/piece	3.2g NBR/piece	**3g NBR/piece**	**2.5g NBR/piece**
Wet ton of latex needed	**11.11**	**10.00**	**8.89**	**7.78**	**7.11**	6.67	5.56
% of savings	N/A	10% from 5g/piece	11% from 4.5g/piece	13% from 4g/piece	9% from 3.5g/piece	6% from 3.2g/piece	17% from 3g/piece

By using **SyNovus™ Plus** latex, gloves can be produced at a **lighter weight with lower curing temperature**, resulting in **increased efficient use of raw materials and saving of energy**

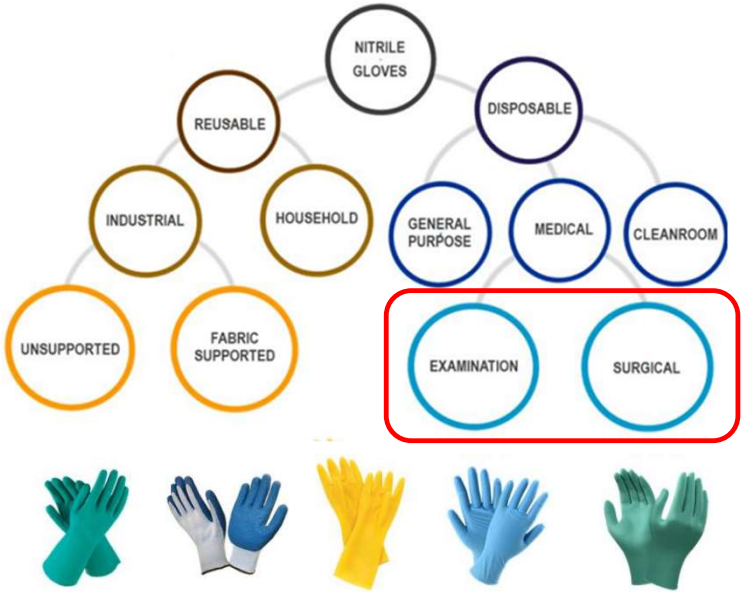
SyNovus™ Plus Technology Platform towards Glove Circular Economy

Sustainability is a core part of Synthomer innovation mindset
using a multi-faceted approach for improving human health and reducing environmental impact with a focus on the complete product value chain and cradle-to-grave product life-cycle analysis



Further Development of SyNovus Technology towards Glove Circular Economy

- In 2020, there was an estimate of >1.7M wet ton of NBR Latex being sold worldwide*. More than **200 billion pieces of NBR gloves** were produced and consumed in 2020
- Bulk of used NBR gloves to be incinerated for low efficiency energy recovery or **dumped as landfill, causing seriously environmental pollution** and **resource waste**
- While keeping the feature of lower energy for curing during glove production, **SyNovus Plus latex was ecologically designed for better sustainability**



Used gloves with Biohazard → Incineration

Other used gloves Off-spec gloves → Landfill

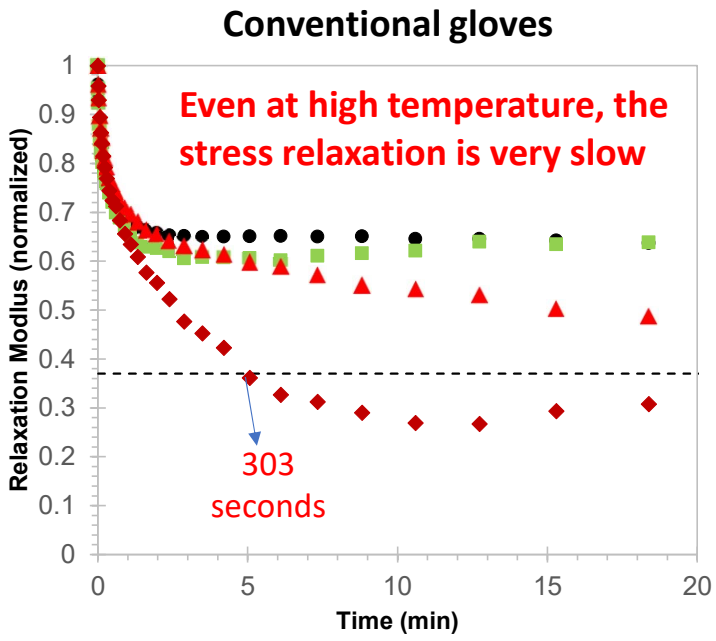
Other used gloves Off-spec gloves → SYNOVUS™ PLUS → Recycle / Reuse (not as gloves)

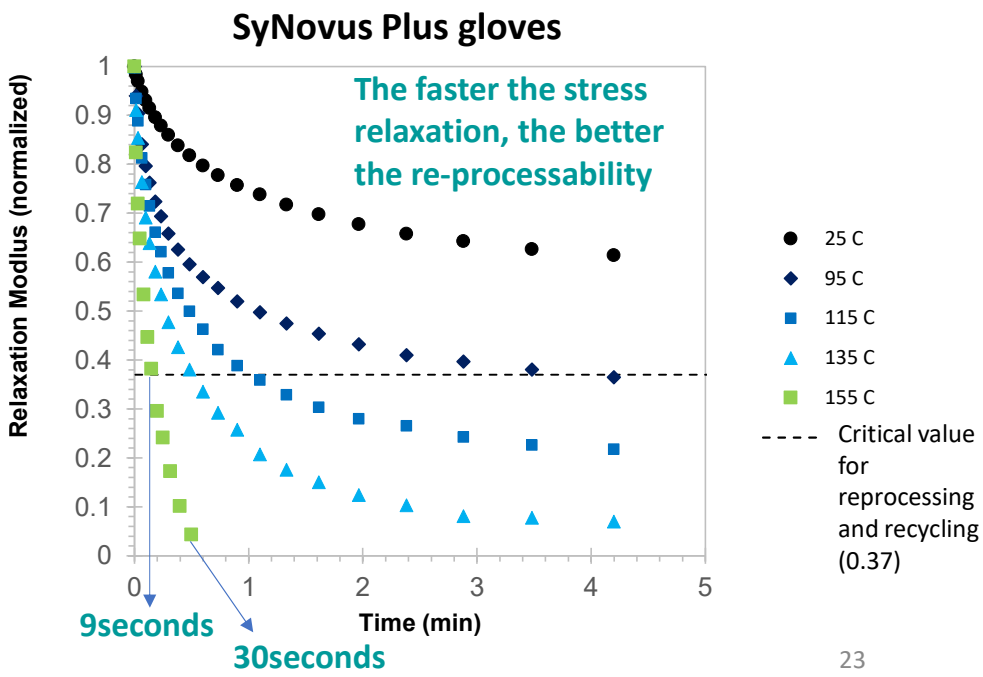
*: https://dataweb.usitc.gov/ and https://www.trademap.org/Index.aspx

Further Development of SyNovus Technology towards Glove Circular Economy

Dynamic Mechanical Analyzer (DMA) study for nitrile glove recyclability

Tests of glove samples confirmed that **SyNovus Plus gloves give very fast stress relaxation profile** which means excellent ability for glove re-processing

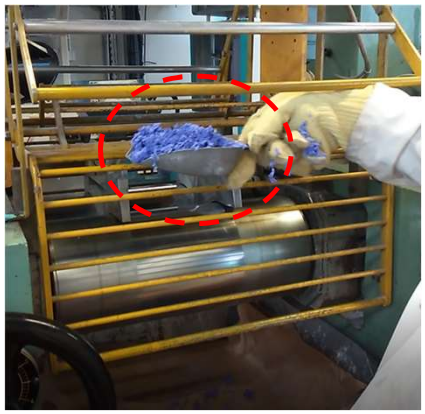




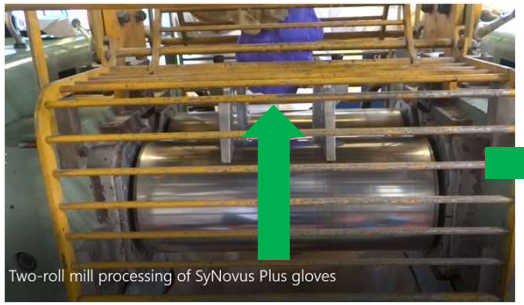
Further Development of SyNovus Technology towards Glove Circular Economy

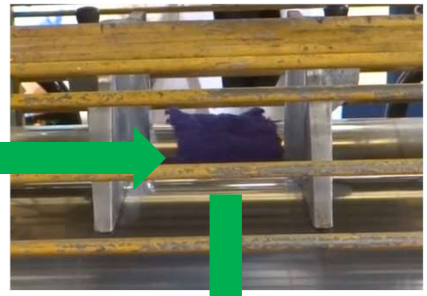
Glove recyclability tests using two-roll mill without additional chemicals

Conventional S-vulcanized gloves failed to form a good sheet even after several minutes of processing at 175°C



SyNovus™ Plus gloves showed very fast sheet formation after processed at 175˚C for ~30s, like the Play-Doh compound passing through the toy processor





Further Development of SyNovus Technology towards Glove Circular Economy

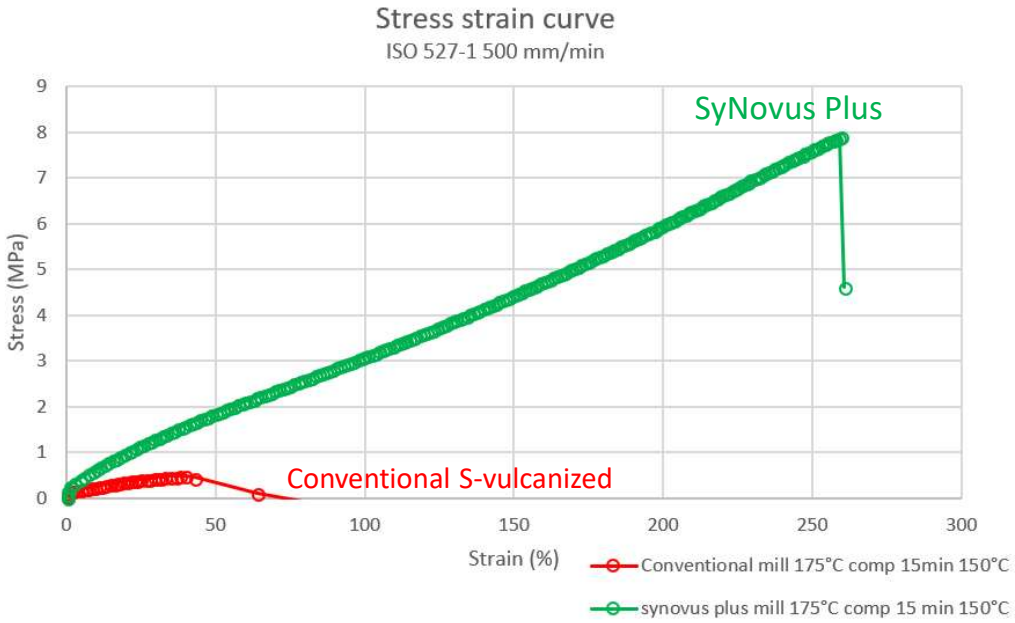
Glove recyclability tests using Compression Molding

From Conventional S-vulcanized gloves

Process at 175˚C with the two-roll mill followed by compression molding at 150˚C for 15 minutes

From SyNovus Plus gloves

Process at 175˚C with the two-roll mill followed by compression molding at 150˚C for 15 minutes



SyNovus Plus gloves could be recycled to

Summary

SYNOVUS™ PLUS

The choice for producing sustainable accelerator-free and readily recyclable nitrile gloves

- Glove producers could use SyNovus Plus latex to make gloves with over-all lower manufacturing costs
- End users prefer SyNovus Plus gloves with low Dermatitis Potential, low odour and soft hand feeling
- SyNovus Plus Technology enables glove circular economy

• Conventional gloves	• Free from rubber accelerator & sulfur • Energy saving	• Even lower carbon footprint • Recycle and Reuse

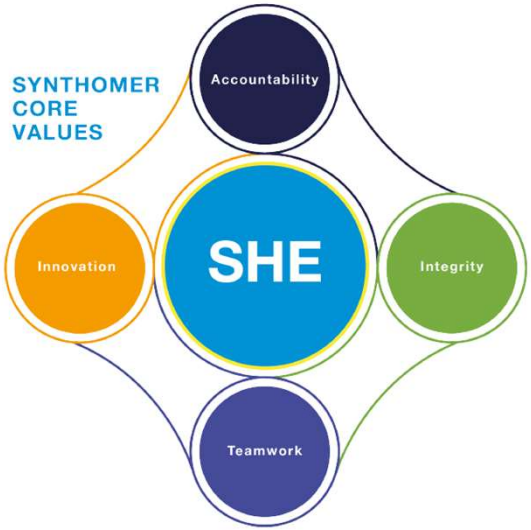
SyNovus Plus

SyNovus

Conventional XNBR Latex

Moving towards the
green future of Nitrile Latex Technology
for protecting end users and environment

Acknowledgements



Innovation Excellence in the **Synthomer** way

We would like to thank all team members involved in SyNovus Plus project

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We need more talents like you to join us !
Please check Synthomer LinkedIn webpage for more information

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SYNOVUS