Research Opportunities in Rubber Glove Industry in Malaysia*

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*For Educational Purposes only

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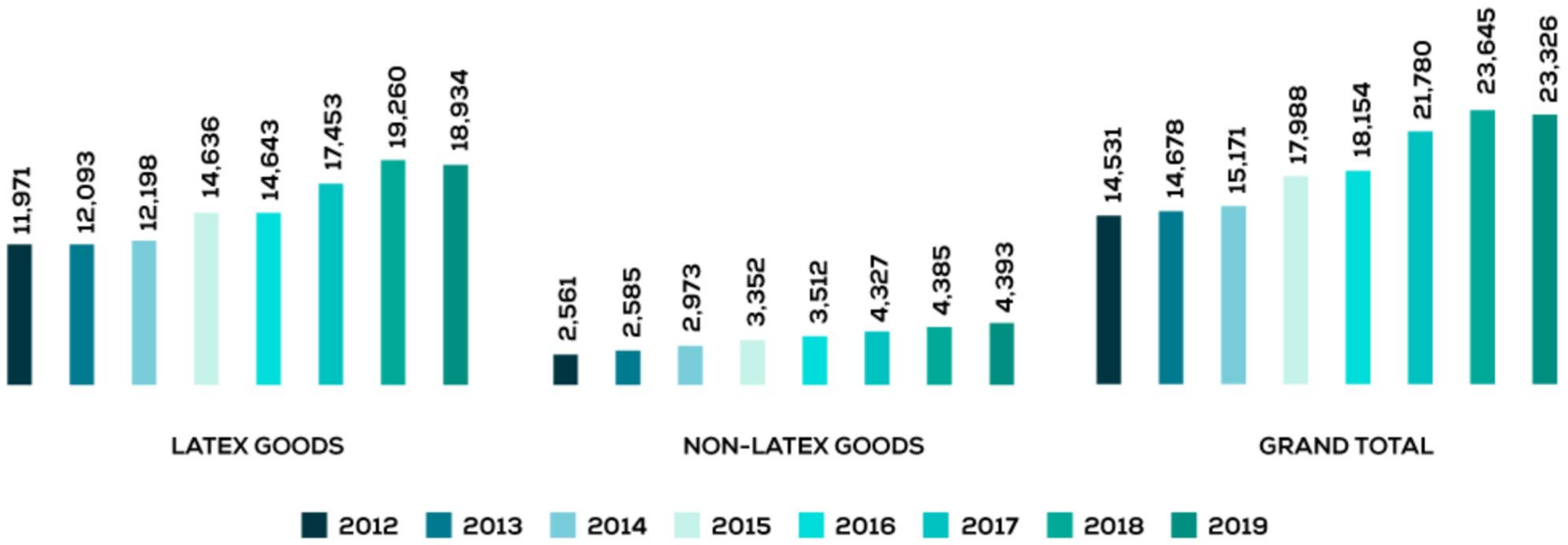
Malaysia's Exports of Rubber Products
From Malaysian Rubber Council's (MRC) website



Source: Department of Statistics (DOS)

Malaysia's Exports of Selected Rubber Products (From MRC)

Rubber Products	Value (RM Million)					
	2014	2015	2016	2017	2018	2019
Gloves, Other Than Surgical Gloves	9,436.5	11,764.8	11,848.8	14,283.8	16,190.6	15,788.5
Surgical Gloves	1,265.4	1,332.2	1,432.6	1,572.0	1,550.7	1,565.0
New Tyres	929.5	1,059.4	1,042.0	1,402.0	1,198.9	1,379.0
Tubes, Pipes and Hoses	520.3	656.3	666.0	843.7	962.9	765.4
Latex Thread	445.6	515.9	520.5	689.8	571.0	536.1
Catheters	428.1	311.2	201.9	195.0	351.1	425.9
Condoms	325.5	431.0	388.5	436.8	338.0	322.1
Seals and Gaskets	93.5	137.3	183.3	201.8	212.1	160.9
Foam Products	96.5	106.9	119.4	132.6	119.1	149.5
Precured Treads	97.7	97.6	95.3	108.7	102.2	114.3
Floor Coverings and Mats	66.9	66.6	82.5	91.9	92.1	91.0

Types of Rubber Gloves (Unsupported)

1) Disposable – a) Medical – i) Examination gloves; ii) Surgical gloves
   b) Non-medical gloves – Examples: i) Cleanroom
   ii) Food handling
   iii) Pharmaceutical / Life Sc
   iv) Janitorial
   v) Hair-dressing
   vi) General purpose
2) Reusable – Non-medical gloves – Examples: i) Chemical resistant gloves
   ii) Automobile
   iii) Agriculture & Fishery
   iv) Semiconductor
   v) Food processing
   vi) Household

Objectives of this 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 from the literature

Typical Glove Processing

- **Latex Compounding**
  - Sulfur
  - Accelerator
  - Antioxidant
  - Activator
  - Surfactant
  - Viscosity modifier
  - Filler
  - Pigment
  - Anti-ozonant
- **Latex Dipping**
  - Straight dipping
  - Coagulant dipping
    - Powdered Coagulant
    - Powder-free Coagulant
  - Heat sensitized dipping
- **Drying & Crosslinking**
  - Sulfur Curing
    - Pre-vulcanization
    - Post-vulcanization
  - Zn Oxide Curing
  - Radical Curing
- **Post processing**

Online Process

Former Loading > Former Cleaning > Drying > Coagulant > Drying > Latex > Dripping > (Second Latex) > Gelling > Beading > Wet Gel Leaching > (Priming) > Polymer Coating > Drying & Curing > Dry Film Leaching > [Chlorination - Neutralization - Rinsing] (Optional) > Silicone/Slurry (Optional) > Stripping > Packaging > Sterilisation

How Its Made -- Rubber Gloves.mp4

Quality Control & Quality Assurance

Raw Materials
- Incoming raw material checking / testing
- Supplier qualification, audit

Compounding
- Solution, dispersion, emulsion preparation
- Mixing of ingredient and maturation / prevulcanisation
- Testing of compounded latex

Dipping
- Parameters, e.g. temperature, pH, flow rate, circulation speed
- Testing, e.g chlorine, calcium nitrate, total solid, viscosity
- In-process quality control check for holes, cosmetic defects

Packaging (Sterilization)
- Testing for packaging and final release criteria

Desirable Research – General Consideration

- Easy operation, preferably no machine modification
- Simplify the production process, e.g. reduce manual operation
- Not costly to produce. Disposable products are cheap. Cost-benefit balance
- Fast return of investment
- Preferably no drug-device combined products, e.g. antimicrobial agent
- Improved product performance
- Preferably working principle / mechanism is known via feasibility study
- Materials commercially available, preferably no nano-materials
- Reduce defects, waste, effluent discharge
- Improve health e.g. skin friendliness, biocompatibility
- Increase through put, reduce time, increase efficiency

This presentation focuses on research related to Polymer & Materials

Manufacturer Requirements

1) Online hole detection

Dipping

- Parameters, e.g. temperature, pH, flow rate, circulation speed
- Testing, e.g chlorine, calcium nitrate, total solid, viscosity
- In-process quality control check for holes, cosmetic defects

- Current status: Perform in process quality control via water leak or air inflation
- Problem: 1) Labour intensive and slow

  2) Based on sampling only. Not all gloves are tested

  3) Water leak tested gloves require drying; inflated glove stretched > may cause damage to the gloves
- If hole in glove can be detected online, it will contribute to:

  1) Cost saving; 2) Time-saving; 3) All gloves are tested

Examples: 1) Physical method; 2) Chemical methods; 3) Other methods

Manufacturer Requirements

2) Curing System

- Current status: Accelerator & sulphur are used for crosslinking
- Problem: 1) Accelerator could cause skin reactions, formation of nitrosamines
  2) Accelerator is cytotoxic, unable to meet ISO10993 Part 5
- Accelerator-free systems: Difficult for natural rubber & polyisoprene latexes
- Nitrile latex – 1) Self crosslinking monomers can be incorporated
  2) Carboxylic acid can be used for ionic crosslinks formation
- Polychloroprene: Zinc oxide as crosslinking agent, reacting with the 1,2-unit
- Alternatives – 1) Peroxide or hydroperoxide curing systems (in molten salt)
  2) Irradiation curing systems, e.g. gamma, UV but poor aging
- Example 1: Peroxide + Irradiation (Nuclear M'sia) – No aging data
- https://www.researchgate.net/publication/334547792_Radiation_dose_required_for_the_vulcanization_of_natural_rubber_latex_via_hybrid_gamma_radiation_and_peroxide_vulcanizations

Manufacturer Requirements

2) Curing System for Polyisoprene and Natural Rubber

Example 2: The invention relates to method for producing a crosslinked elastomer by radiating a polymer dispersion of at least one crosslinkable polymer with electromagnetic radiation in the ultraviolet (UV light) and/or visible spectral range, wherein the crosslinking is performed in at least two stages as pre-crosslinking and post-crosslinking and at least one photoinitiator is added to the polymer dispersion to trigger the crosslinking reaction prior to the pre-crosslinking. At least one photoinitiator is added once again to the pre-crosslinked polymer dispersion prior to and/or during the post-crosslinking, and the post-crosslinking is also performed with electromagnetic radiation in the ultraviolet (UV light) and/or visible spectral range.

Method for producing a cross-linked elastomer US Patent 8673993 (2014)

Manufacturer Requirements

3) Powder-free System

- Coagulant normally contains powder (calcium carbonate) for producing powdered glove or washed off in post processing step, e.g. chlorination
- Current status: Metal stearates, e.g. stearates of potassium, calcium, and zinc are also used in coagulant to produce powder-free gloves

Problems: a) Stearates are not good enough to produce a good slip surface for double gloving
b) Former contamination and wetting are still the issues.

- A new powder free glove production system is desirable

Example: The emulsion polymerization of nitrile latex was conducted in presence of a degraded polysaccharide having a DE (Dextrose Equivalent) of 2 to 90 measured according to ISO 5377. The glove made from this latex does not require surface treatments (both inside & outside!). US Patent 10,377,882 (August 13, 2019)

Manufacturer Requirements

4) Thin Natural Rubber (NR) Examination Glove

- Gloves are sold by pieces, not by weight
- Thinner gloves reduce product cost, provide good sensitivity to user
- Current status: Nitrile gloves can be as thin as ≈ 0.04mm
- Problem: a) Natural rubber gloves are much thicker, around ≈ 0.06mm
  b) Lower thickness NR glove tends to have thin spot and film issues
- Thinner NR gloves will be well received by the industry
- Reason for NR gloves being thick: Possibly larger particle size
- Particle size of nitrile is 8-10 times smaller than NR latex
- NR condoms can be thin due to the symmetrical shape of the product
- For gloves, may have to use different types of former material, or additives to improve film formation

Manufacturer Requirements

5) 100% Prevulcanised Synthetic Latexes

- A 100% prevulcanised latex does not require vulcanisation during product processing.
- This saves time and simplifies production process.
- Particularly useful for small manufacturer
- Also for export to countries where the rubber chemicals are not readily available.
- Problem: a) Only NR latex can be 100% prevulcanised & commercially available
  b) All synthetic latexes have yet to achieve 100% prevulcanisation
- Due to stiff chain after curing in latex and high surfactant in synthetic latex
- Synthetic polyisoprene is as soft as NR but the properties are different (high surfactant, narrow particle size distribution, narrow molecular weight distribution)

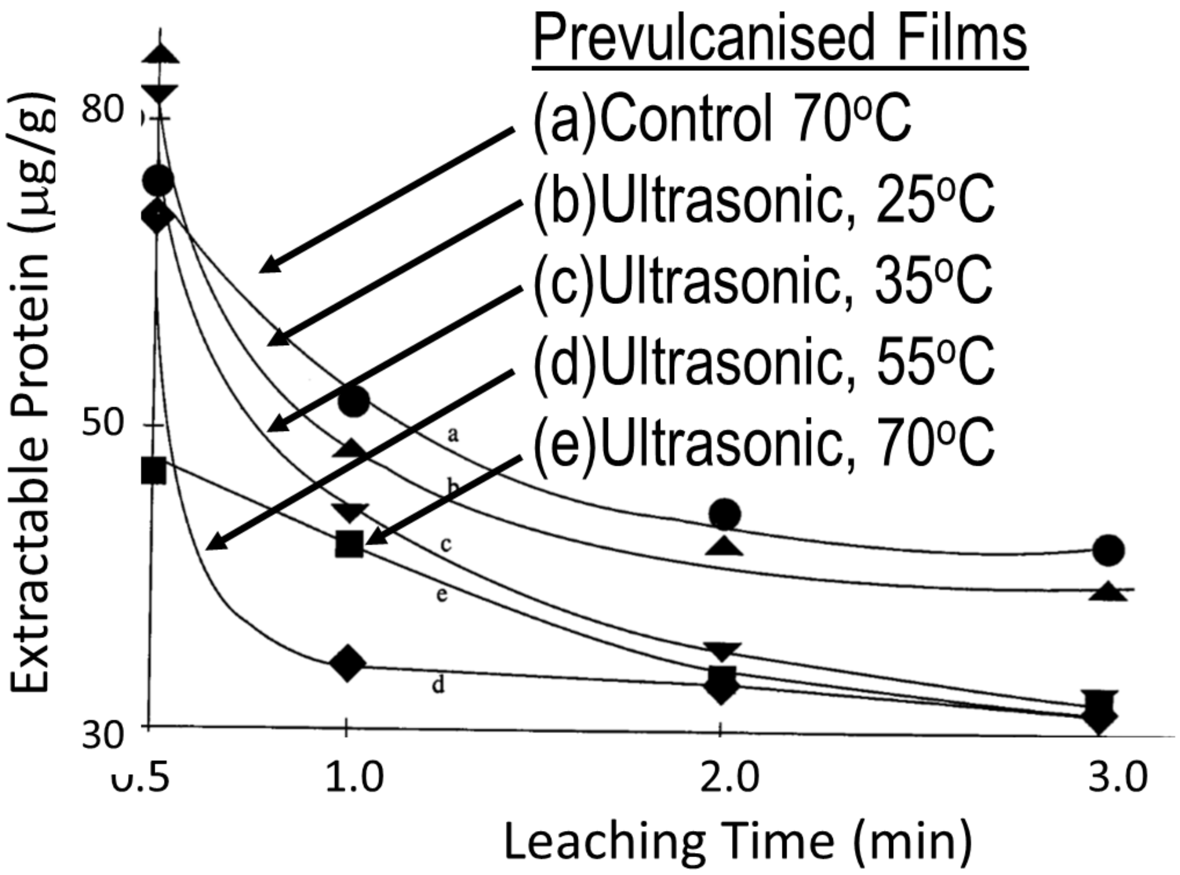
Manufacturer Requirements

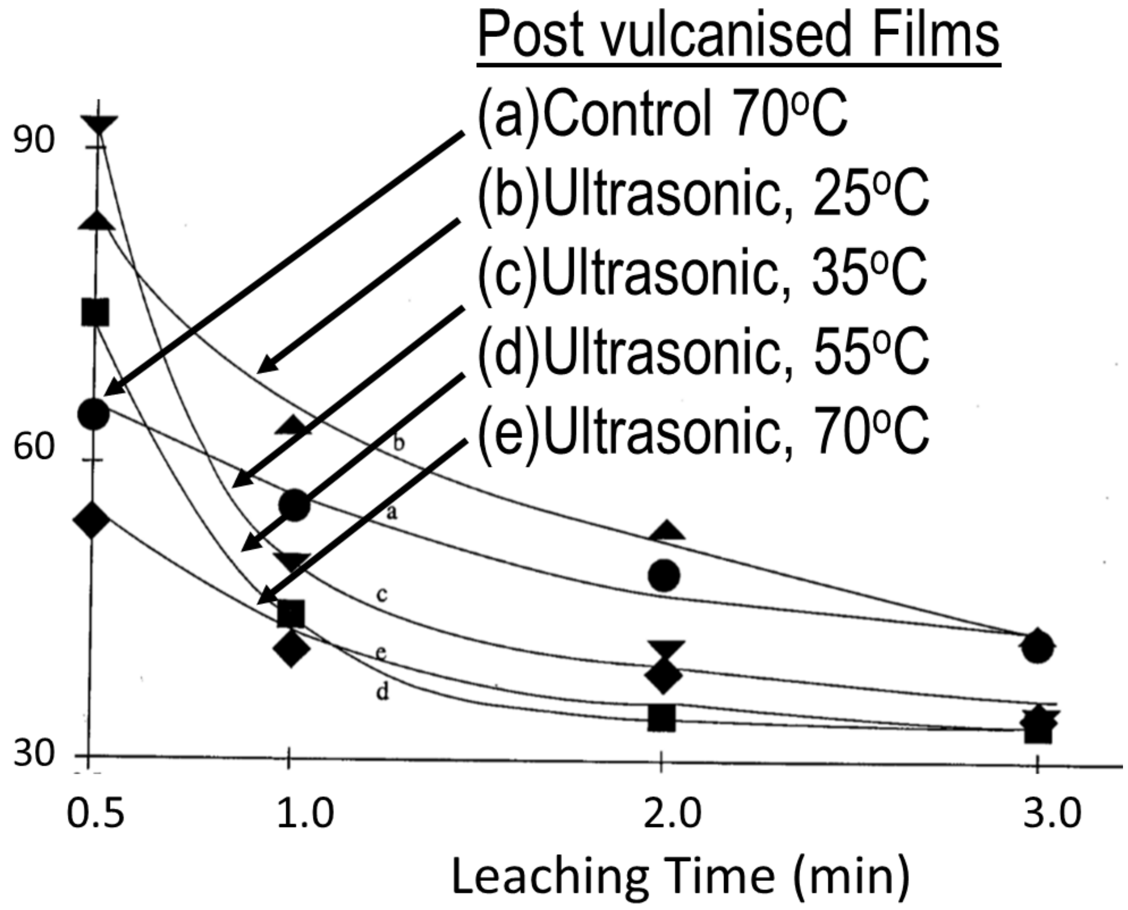
6) Efficient Leaching System

- Leaching, a cleaning process, removes unwanted non-rubber materials, such as surfactants, proteins, coagulant
- Less odour, lower skin unfriendly materials, e.g. accelerator, proteins
- Also promotes inter-particle integration > improves tensile properties
- Current status: 1) Two stages: Before curing (pre-leach, 50-70^{o}C) and after
- curing (post-leach, 80-90^{o}C)

  2) Continuous topping up of fresh water, draining dirty water
- Problem: Consumes water and power
- A higher efficiency leaching reduces water and power consumption
- Better efficiency at high temperature, agitation, slightly higher pH, correct flow
- Are there other methods of high efficiency leaching ? Fast removal of solubles

Example: Dry film ultrasonic leaching (Post leach)





Journal of Rubber Research (1999) 2(1):23-28

http://vitaldoc.lgm.gov.my:8060/vital/access/services/Download/vital1:23736/ARTICLE

Manufacturer Requirements

7) Improving Tensile Strength of Polyisoprene

- Polyisoprene latex of anionic polymerisation origin is difficult to cure to optimum tensile strength
- Problem: 1) A high level of curing agent, such as accelerator is normally used.
  2) High residual accelerator in products may give unpleasant smell and may also cause skin allergy to sensitive individuals

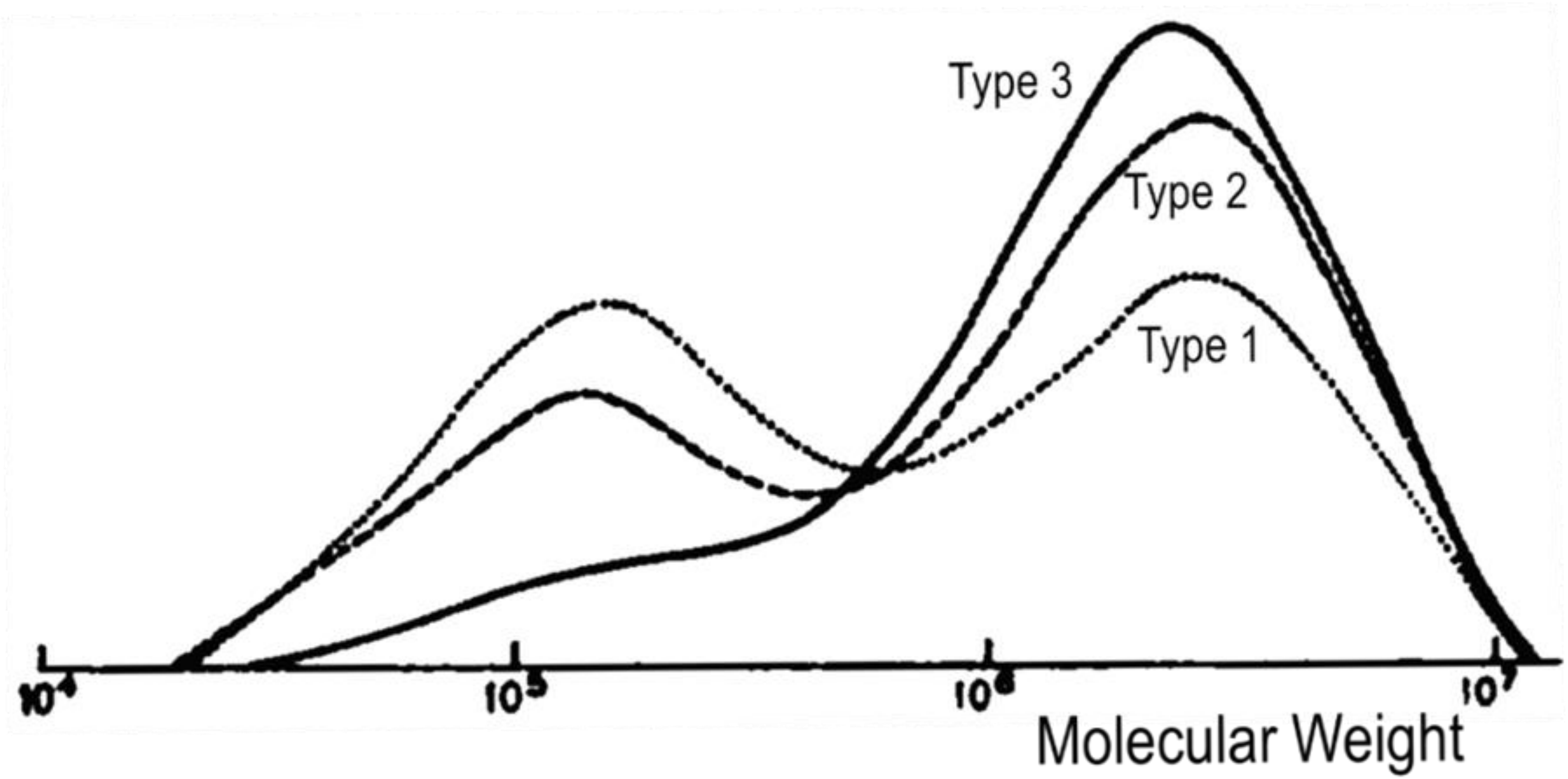
Example: A synthetic polyisoprene latex containing synthetic polyisoprene, wherein the synthetic polyisoprene constituting the synthetic polyisoprene latex includes a low-molecular weight synthetic isoprene chain having a molecular weight of less than 1,000,000 at a content rate of 10 to 70% by weight and a high-molecular weight synthetic isoprene chain having a molecular weight of 1,000,000 or more at a content rate of 30 to 90% by weight.

US Patent App. 20200062873

Manufacturer Requirements

7) Improving Tensile Strength of Polyisoprene

Molecular weight distribution of natural rubber



Manufacturer Requirements

8) Test Method Development

- Objective (measureable) test methods for

a) Donnability, dry hand and damp hand

Current method: Subjective donning test

Problem: 1) Damp hand conditions difficult to measure

2) Restricted by hand size (too small & too big sizes)

b) Durability

Current method: Tensile test / shelf life

Problem: The test is not well correlated with durability during actual use

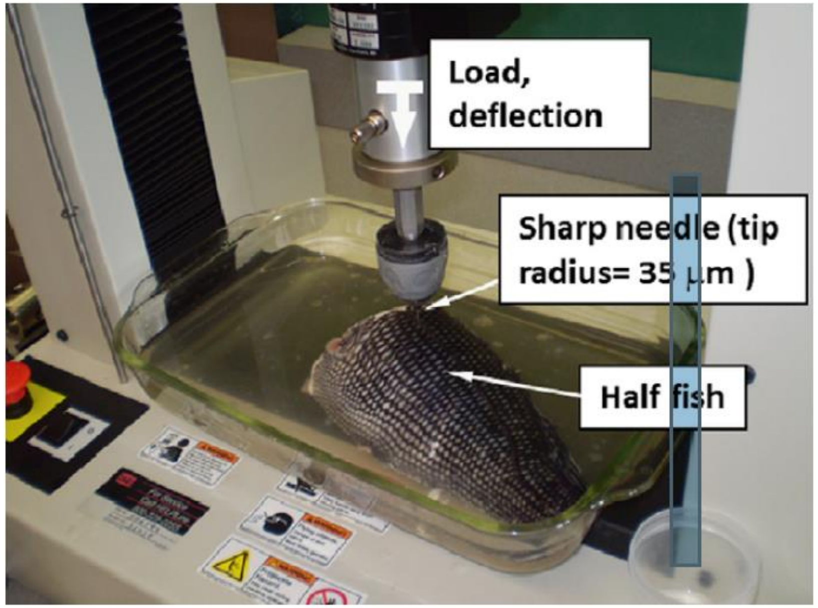
c) Grip, dry and wet grip

User Requirements of Medical Gloves

1) Puncture resistance against hypodermic needles (Test method ASTMF2878) to prevent needle stick injury during use

- Cases of needle stick injury in healthcare settings are common
- Current status: No medical glove can withstand sharp needle puncture.
- Needle puncture resistance force of 2N (25G, 0.52mm diameter) minimum

a



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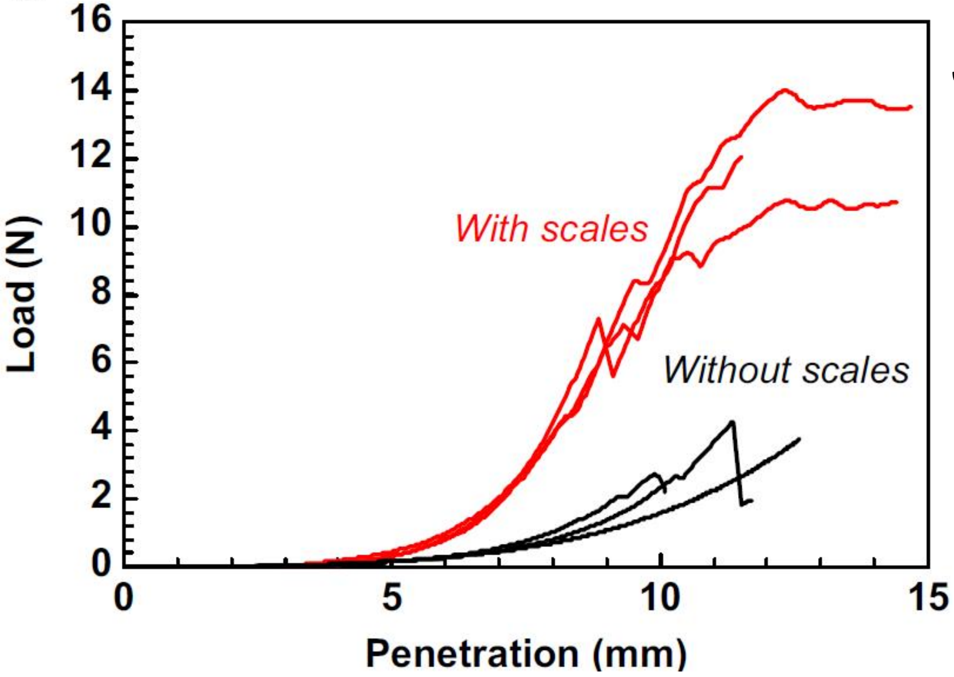


Journal of Mechanical Behavior of Biomedical Materials (2013), 24, 30–40

User Requirements of Medical Gloves

2) Bone cement (acrylic monomer) resistance

- Bone cement is used to hold broken bone in shape by orthopaedic surgeons
- Current status: 1) No medical glove in the market can prevent permeation of bone cement (Usually permeate in less than 10 minutes).
  2) User who are allergic to bone cement normally wears 2-3 gloves and changes regularly to prevent permeation
- Problem: 1) Frequent replacement of surgical glove interrupts the medical procedure
  2) Some users are allergic to bone cement
- A bone cement resistant glove is expected to be well received by the user

User Requirements of Medical Gloves

3) Damp hand donnable

- Healthcare worker needs to wash hands before wearing and after doffing the gloves
- The hand may be damp when donning the glove, normally difficult to don
- Wet hand donning is normally not practised > uncomfortable
- Current status: Surfactant is used for damp hand donnable properties.
- Problems: Some users are allergic to certain surfactants.
  Some surfactants are endocrine disruptor (Not complying with REACH)
- Glove’s surface that is good for damp hand donning:
  1) High surface roughness (micro roughness: reduce contact with skin)
  2) Hard surface
  3) Lubricating when it is moist

User Requirements of Medical Gloves

4) Improving tear resistance of synthetic gloves

- Tearing during glove donning is one of the common problems
- Current status: Most synthetic gloves, such as synthetic polyisoprene and nitrile gloves, have a poorer tear resistance property than NR glove

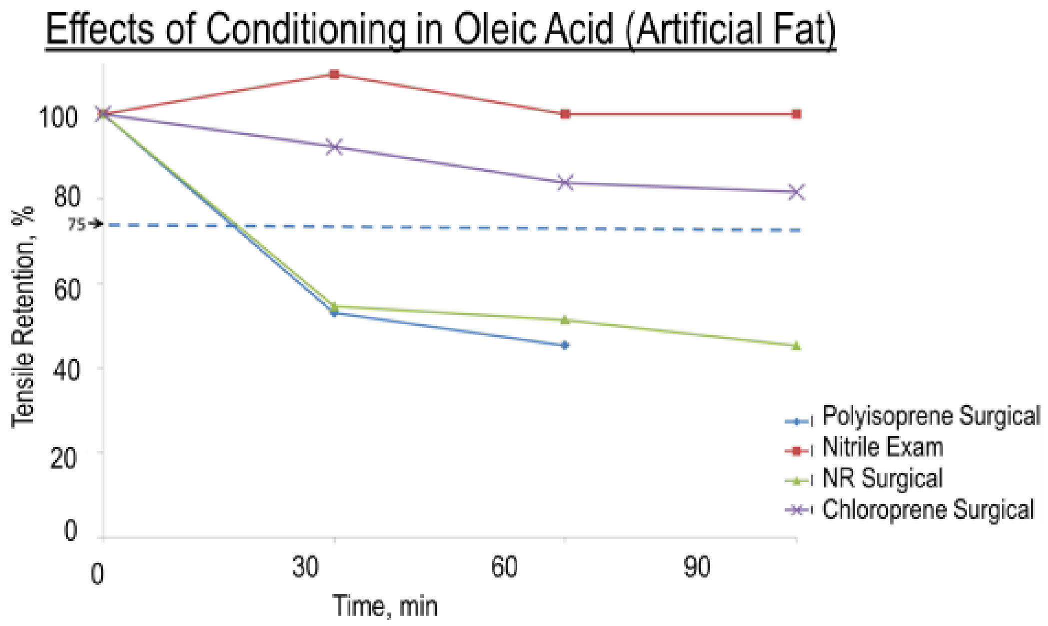
- Example: A latex composition containing a conjugated diene polymer latex and a medium-chain fatty acid glyceride, wherein a content proportion of the medium-chain fatty acid glyceride is 1 to 40 parts by weight with respect to 100 parts by weight of the conjugated diene polymer. In the present invention, a medium-chain fatty acid forming the medium-chain fatty acid glyceride is preferably a fatty acid having 6 to 18 carbon atoms. In the present invention, the medium-chain fatty acid glyceride is preferably a medium-chain fatty acid triglyceride. The latex composition preferably further contains a crosslinking agent.

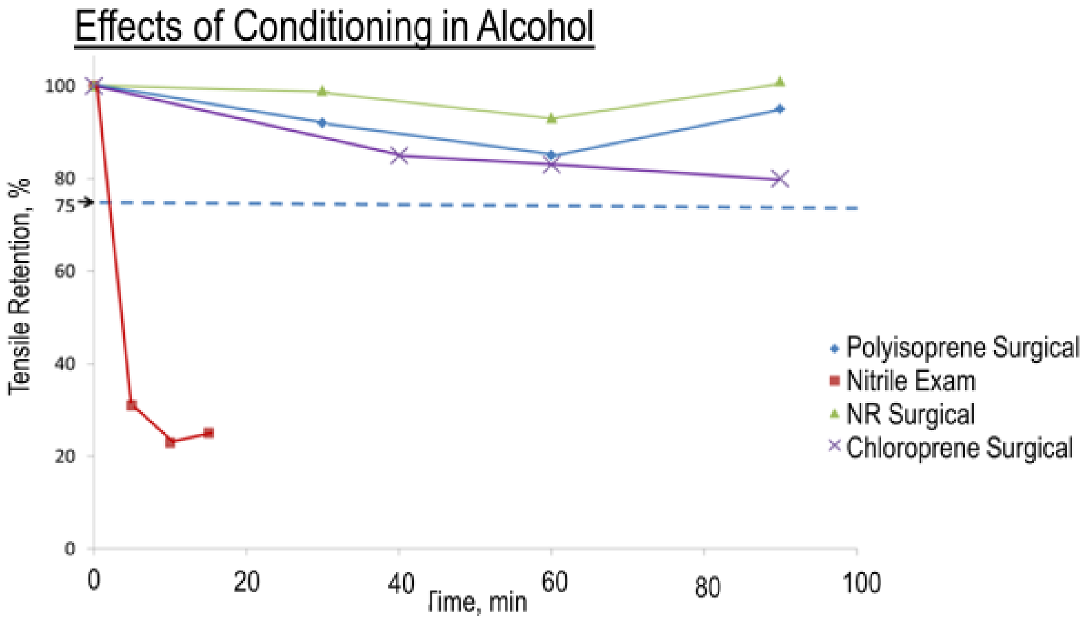
US Patent App. 20190300685* Claims on Polyisoprene, SIS, Nitrile

User Requirements of Medical Gloves

5) Improving oil / fat resistance of natural rubber /Polyisoprene gloves and alcohol resistance of nitrile glove

- Natural rubber is a non-polar polymer, weak against oil / fat
- Nitrile rubber is relatively polar, weak against alcohol
- Improving the oil resistance will enhance the NR glove safety & durability
- Improving alcohol resistance will enhance the nitrile glove safety and durability





Chemistry in Malaysia September 2015, Page 4-8

User Requirements of Medical Gloves

6) Better breach detection

- A breach detection system alerts the user when the glove is breached.
- Most of the users are unaware of glove breach during use.
- Current status: Combination of darker under glove and brighter outer glove. A breach will be detected when liquid penetrates through the hole and the colour of wetted under glove become more visible.
- A better breach detection to inform the user glove breach during use

Example: A surgical glove has inner and outer surfaces. At least one of the surfaces is treated with a treatment consisting of a non-ionic hydrocarbon solution with a carbon chain in the range of 8-16 and containing a hydrophilic functionality with a pH within the range 4.5-6.5. After treatment, the treated surface or surfaces are dried, the glove packaged and then irradiated. The treatment controls the initial contact angle of the surface to be less than 70 degrees, so that liquid material will spread quickly across the treated surface or surfaces, thereby ensuring that the presence of the liquid, indicative of the glove having been compromised, is visible to the wearer or other observer as quickly as possible.

Puncture indicating gloves US Patent 9308048

User Requirements of Medical Gloves

7) Glove with super hydrophobic surface (will not be soiled during used)

- Improves visibility of gloved fingers during a procedure, e.g. stitching
- Reduce or prevent contact transfer of pathogens from surface to surface
- Current status: No such glove in the market

Example**:** The article contains an elastomeric base and a fluid-repellent coating composition that effectively repels both hydrophilic and lipophilic liquids from its surface and inhibits cross-contamination of surfaces. Articles prepared in accordance with the invention reduce the risk of contamination associated with blood and other body fluids, as well as reduce fluid-based visual obstruction and enhance the clarity of medical procedures

Repellent elastomeric article , US Patent 8,530,016 Sept 10, 2013

User Requirements of Medical Gloves

8) Improve comfort

- Sweat reduces the comfort of glove use
- Ability to remove / reduce sweat of user during use, improves comfort
- Either through absorption or transmission (e.g. polyurethane)

Example: A disposable surgical glove comprising a first thin elastomeric layer (1); and a second layer (3) to having a securely bonded, or laminated fabric liner (3) so that the second layer (3) is configured to absorb, excess perspiration or moisture of the skin, wherein both layers (1) (3) are held evenly together by a coagulant and bonded by an adhesive chemical, such that the elastomeric glove (1) and fabric liner (3) may be stretched to whatever extent, without affecting its lamination, and method of manufacturing with the use of a skeletal rubber former (2).

World Intellectual Property Organization WO2010107297 23 September 2010

User Requirements of Medical Gloves

9) Replacement of chlorine for surface treatment

- Current status: Chlorine is used to reduce the surface tackiness / stickiness of glove (Materials are of low glass transition temperature).
- No chlorine alternative for producing cleanroom gloves
- Problem: 1) Chlorine is toxic,
  2) Chlorinated compounds may be toxic, e.g. dioxin
  3) Chlorination is difficult to control and handle
  4) Chlorination may cause degradation to rubber
  5) Chlorination may cause discolouration to glove
  6) Change of grip on storage (turns slippery)
  7) Polychloroprene is not very reactive to chlorine
- Any good alternative to chlorine for surface treatment will be welcomed by the industry

Concluding Remarks

- Glove manufacturing process is 50% science and 50% art
- The art part is normally kept as a trade secret
- The science part is not fully understood
- The performance of glove is determined by material properties as well as glove integrity such as presence of thin spot, holes, dirt.
- There are many more areas of research opportunities in the industry
- This presentation only highlighted a few related to polymer & materials
- More information on this area can be obtained by discussing with the manufacturers and users

End of Presentation
Thank you