CURRENT TRENDS IN LATEX DIPPED GOODS INDUSTRY

Prof. Dr. Ho Che Cheong
University Tunku Abdul Rahman

Abstract

Hevea natural rubber (NR) latex has been the only feedstock for medical glove manufacturing for a long time until the issue of rubber latex protein allergy emerged in the late 1980s when a dramatic surge in the use of and increased exposure to medical barrier device made from natural rubber latex triggered the onset of the increased instances of allergy to rubber proteins, in particular to sensitized users. This was brought about by the outbreak of the pandemic AIDS/HIV and a mandatory use of infection control in healthcare environment. The frantic search for a suitable alternative to Hevea latex ensued in the 1990s when more cases of allergy to NR proteins were reported in the developed economies where gloves were extensively used as a barrier device.

Since synthetic polymers were already widely used in many applications, it was natural to search for synthetic latex that can mimic the properties of NR in glove applications. Unfortunately there was no synthetic latex found to be suitable for dipping to produce a functional glove piece in the beginning (late 1980s). Synthetic latex was not made for dipping purpose and the polymer making up the latex particles did not form elastic film that can meet the application requirement of a barrier against infection. The closest was acrylonitrile butadiene (NBR) latex. However examination gloves made from this latex was far inferior in properties compared to NR gloves. The ensuing next three decades, manufacturers of NBR latex have modified and improved the properties of the NBR latex to a remarkable level thereby narrowing the gap between the properties of preferred NR glove and those of a non-Hevea alternative. At the same time several synthetic latexes made up elastomers such as polychloroprene, cis-polyisoprene and more recently thermoplastic elastomers such as SIS have emerged which mimic the properties of NR gloves but none are able yet to match the superior properties of NR gloves.

This presentation provides a brief review of the development of new latex materials suitable for glove dipping and possessing the necessary pre-requisites in barrier application; the intense search for benign alternatives of rubber chemicals to replace those obnoxious and toxic conventional accelerators and biocides; the trend of employing eco-friendly processing and increased use of automation in processing, including energy conservation and efficient usage, minimizing waste water generation and increased effort in water recycling; greater emphasis on material conservation and thinner gloves; greater productivity via innovation in dipping-line design for faster chain speed and maintaining zero rejects. The impact of digital revolution and Industry 4.0 on latex dipping industry will be briefly described.
Current Trends in Latex Dipped Goods Industry

C. C. Ho
University Tunku Abdul Rahman

Outline

• Pre-requisites of latex film as barrier material
• Understanding basics of latex dipping
• New latex development (feedstock) for dipping
• Prudent usage of chemicals in latex dipping
• Addressing safety, sustainability and eco-friendliness issues
• Recent development
Pre-requisites for latex film as barrier material

Application Properties of medical gloves for infection control

- Good grip for working surface
- Soft and conform to contour of hand
- Mechanically strong (stretchable) and elastic (non-deformable)
- Donnable as a glove: low surface friction against skin
- Barrier properties: Continuous (impervious) film for protection against pathogens and microbes
Criteria for Latex choice in glove dipping

- Readily available commercially for dipping industry
- Suitable and stable for high-speed online dipping
- Impervious film formation (infection protection)
- Dipped film mechanically strong, highly elastic
- Donnable, good grip, contour conforming and comfort
- Reliable and acceptance by industry

Traditionally ..... 

- NR *Hevea* latex was the only feedstock for glove dipping: high tensile and elasticity, low modulus, excellent recovery properties
- Good film forming: excellent barrier protection
- High tactile sensitivity
- Properties unsurpassed by synthetic latexes
Search for synthetic alternatives began...

- Triggered by discovery and reports of allergies linked to latex proteins from NR gloves following increased usage of medical gloves by healthcare workers in 1980s (Type I allergy)
- Traced to latex proteins adhered to air-borne powder from glove
- Residual latex proteins in poorly leached gloves cause allergic reaction in certain sensitized users

Emergence of synthetic latexes for gloves

- Mostly manufactured directly by emulsion polymerization
- Method used as route to obtain solid synthetic rubbers
- Polychloroprene latex and NBR (nitrile) latex prepared directly by emulsion polymerization
- Synthetic *cis* polyisoprene latexes are artificial latexes
- Latex contains high surfactant contents
- Require different curing system and process
- Limited latexes suitable for glove dipping then
Possible choice of latex type ...

- Natural rubber - *Hevea* latex (well-established)
- Synthetic alternatives
  1. Synthetic latex
     - recent new comers for dipping application
     - few suitable choices via synthetic route
     - petroleum-based
  2. via Biomass route for monomers e.g. isoprene from bio-refinery (*developmental*)
- Non-*Hevea* latex-producing plants: guayule and Russian dandelion latex (*developmental*)

Molecular structure-property relationship

- High molecular weight - entanglement of polymer chains: straight and branched, ease of alignment of polymer chains on extension by stretching
- Readily cross-linkable:
  - unsaturated C=C bonds, COO⁻ groups allow x-linking and network formation, confer strength and elasticity
- Continuous matrix (soft) and microdomains (hard)
- Soft and low $T_g$ materials promote film forming
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Commercial synthetic latexes suitable for medical glove dipping

- Acrylonitrile butadiene (NBR) latex
- Synthetic *cis* polyisoprene latex (artificial latex)
- Polychloroprene latex
- Thermoplastic elastomer (triblock copolymer): Styrene-isoprene-styrene latex (artificial latex) - developmental

<table>
<thead>
<tr>
<th>Properties</th>
<th>NR</th>
<th>NBR</th>
<th>ZN-PI</th>
<th>ALi-PI</th>
<th>CR</th>
</tr>
</thead>
<tbody>
<tr>
<td>Curing system</td>
<td>Sulphur</td>
<td>Sulphur and metal oxides <strong>Acce-free</strong></td>
<td>Sulphur</td>
<td>Sulphur</td>
<td>Sulphur &amp; Metal oxides <strong>Acce-free</strong></td>
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<tr>
<td>Mol Structure</td>
<td>Branched</td>
<td>Branched</td>
<td>Branched</td>
<td>Linear</td>
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<tr>
<td>Cis content</td>
<td>&gt;=99 % cis</td>
<td>mostly trans</td>
<td>96+ % cis</td>
<td>90+ % cis</td>
<td>trans</td>
</tr>
<tr>
<td>Gel content</td>
<td>High</td>
<td>Low to high</td>
<td>10-20%</td>
<td>none</td>
<td>Medium-low</td>
</tr>
<tr>
<td>MWD</td>
<td>Wide, high MW</td>
<td>Wide, medium MW 10^6</td>
<td>Narrow, High MW</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Impurities</td>
<td>Proteins, non-rubbers</td>
<td>By-products of polyrn</td>
<td>Catalyst, residues</td>
<td>Low</td>
<td>By-products of polyrn</td>
</tr>
<tr>
<td>Chemical resistance</td>
<td>Poor</td>
<td>Good</td>
<td>Poor</td>
<td>Poor</td>
<td>Good</td>
</tr>
<tr>
<td>(organic non-polar solvents)</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>applications</td>
<td>Exam and surgical</td>
<td>Exam</td>
<td>Surgical</td>
<td>Surgical</td>
<td>Surgical</td>
</tr>
</tbody>
</table>

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Chemicals for latex dipping

To convert latex into final product, requires...

- Stabilization of latex against coagulation: during storage and processing
- Preservatives and protective agents essential
- Curatives to effect cross-linking of rubber molecules (vulcanization)
- Chemicals and additives to facilitate processing
- Property enhancement on functionality
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Chemicals for latex compound

- Surfactants, stabilizers, emulsifiers, wetting agents
- Vulcanizing chemicals (latex compounding)
  - cross-linking agent (most common sulfur)
  - organic accelerators
  - activator (zinc oxide)
- Anti-oxidants, anti-ozonants, waxes
- Biocides and anti-degradants
- Fillers, pigments
- Softening agents and plasticizers

Issues with chemicals used in latex dipping

- Some toxic (to human) e.g. organic accelerators, latex biocides
- Some are carcinogenic, mutagenic, reprotoxic (CMR agents) e.g. ETU fungicides, TMTD
- Some harmful to environment (ecotoxic) e.g. ZnO
- Some are fine powder, creates aerosols (air-borne particles)
- Some are allergens: contact dermatitics

ETU: ethylthiourea
TMTD: tetramethylthiuramdisulfide
Strategies in reducing impact of chemicals in latex dipping

Strategies in mitigation ...

- New synthetic latex: does not require sulfur vulcanization
- Benign alternatives: eliminate e.g. nitrosamine, TMTD, ETU (CMR agents and allergens); reduce or eliminate chlorine, ammonia and zinc usage
- Powder-free: eliminate air-borne particulates
- Material conservation: more effective and efficient usage of materials e.g. thinner gloves; nano materials: effective at lower dosage
- Efficient energy usage and conservation
- Zero waste and water recycling

ETU: ethylthiourea
TMTD: tetramethylthiuramdisulfide
Current trends in latex dipped goods industry

Some commonly used accelerators

<table>
<thead>
<tr>
<th>Thiurams</th>
<th>Thiazoles</th>
<th>dithiocarbamates</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tetramethylthiuram disulphide (TMTD)</td>
<td>Zinc mercaptobenzothiazole (ZMBT)</td>
<td>Zinc dibutyldithiocarbamate (ZDBC)</td>
</tr>
<tr>
<td>Tetraethylthiuram disulphide (TETD)</td>
<td>mercaptobenzothiazole (MBT)</td>
<td>Zinc dimethyldithiocarbamate (ZDMC)</td>
</tr>
<tr>
<td></td>
<td>Benzothiazyl disulphide (MBTS)</td>
<td>Zinc diethylidithiocarbamate (ZDEC)</td>
</tr>
<tr>
<td></td>
<td>Zinc mercaptobenzimidazole (ZMBI)</td>
<td>Zinc pentamethylenedithiocarbamate (ZPMC)</td>
</tr>
</tbody>
</table>

Thiurams, thiazoles, dithiocarbamates cause Type 4 allergy; Commonly used for vulcanization of NR, NBR, syn PI, CP latexes

Non-sulfur crosslinking...

- accelerator-free and sulfur-free: Eliminate use of organic accelerators: mitigate contact dermatitis (Type IV chemical allergy)
- Alternatives to sulfur crosslinking
  - metal oxide crosslinks e.g. zinc oxide, MgO
  - xNBR latex pre-mixed with methacrylic acid
  - use of fugitive accelerator
  - aluminate salt in conjunction with PEG and dialdehyde
  - negatively charged trivalent metal ions at specific alkaline pH≥9.0
Proposed mechanism of sulfur-free crosslinking of NBR molecules

Synthetic latexes for dipping medical gloves

- NBR latex: a workable alternative to NR for exam gloves, cheapest synthetic latex
- Synthetic cis PI (Ziegler-Natta process): artificial latex - workable alternative for surgical gloves, expensive
- Synthetic cis PI (Alkyl Li, anionic polymerized): artificial latex - workable alternative for surgical gloves, expensive
- CP latex - surgical gloves
- PU latex - environmental issues, poor barrier properties
- SIS latex - new comer, new concept, developmental
Advances in synthetic latexes for glove dipping

- Remarkable improvement in synthetic latex properties for glove dipping in the last two to three decades (specifically NBR latex)
- Synthetic latex is protein-free but contains high surfactant contents for stabilization
- Stability control different from NR latex
- Requires different vulcanization system and process
- Vulcanizates not as extensively leached, residues may cause Type IV allergy
- Vulcanize properties vastly improved, narrowing quality gap between NR and synthetic gloves
- Very thin NBR latex film can be produced by dipping
- Malaysia a major NBR exam gloves exporter
- Number of medical gloves dipped from synthetic latexes is ever increasing and encroaching into NR glove market share

Product safety considerations

- Type I allergy due to latex proteins
- Type IV allergy due rubber chemicals
- Protection against bacteria and viruses
- Minimise/eliminate use of known CMR agents
- Powder content: aerosol
- Physical properties
- Nitrosamines (balloons, condoms)
- Compliance with buyers specifications and importing country’s regulatory requirements
Current Trend latex dipping

Trend towards benign chemicals

- Elimination of ammonia as preservative
- Eliminate and reduce use of organic accelerators
- Nitrosamine-free accelerators – safer products
- Benign preservatives, anti-oxidants
- Reduces latex protein products
- Reduce use of zinc oxide
  - reduce waste water treatment
  - decrease impact on environment
Current trends in latex dipped goods industry

### Thinner gloves

- NBR medical gloves weight reduced to 3 g without compromising on quality and safety (~ 0.05 mm thickness)
- Natural rubber latex gloves reduced to 5 g
- Lower cost on latex
- Conservation on material usage
- Lower processing cost
- Lower waste treatment cost

### Other latex dipped goods

- Condom, balloon, finger cots, catheters, baby soothers, etc
- Similar requirement e.g. on nitrosamines-free balloons and baby soothers by some customers and contact allergy
- Same principle on non-sulfur crosslinks can be applied
- Product quality depends on extent of both covalent and ionic bonding in crosslinking NBR molecules
Impact of Industry 4.0

- Smart factory concept: control-centric optimization and intelligence
- Machines as connected collaborative community
- Rapid decision-making
- Big data management in manufacturing
- Cyber-physical system: ability to monitor, share and manage information and action in real world
- Predictive technologies – product performance and service needs

Thank you