Production method & market trend of rubber gloves

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INTRODUCTION
As a device for protecting the hands, rubber gloves afford protection not only against physical and chemical injury but also against infection by viruses and bacteria. They are indispensable everyday items which many of us undoubtedly use in the workplace or at home. This review looks at methods of manufacturing the ubiquitous rubber glove and notes market trends.

VARIETIES OF RUBBER GLOVE
Rubber gloves have been developed for specific usage environments or requirements and there are hence many diverse kinds of rubber glove, here classified according to type in Table 1.

Rubber gloves may be divided into five types. They may be further differentiated according to kind of textile, gauge number of the fabric lining, type of rubber, and treatment of the rubber surface, all of these differences multiplying the kinds of glove in existence.

Although many different kinds of rubber glove are made, they all have one feature in common: the formation of a rubber film matched to the complicated shape of the hand.

RUBBER GLOVE STARTING MATERIALS AND COMPOUNDING CHEMICALS
Rubber gloves are manufactured by dipping a former that mimics the shape of a hand (to make glove types that have a lining, the former is fitted with a woven glove) in a liquid “compounded latex”, and then drying. By way of example, Figure 1 shows the fabrication sequence for rubber gloves of the simplest, unsupported form.

The general manufacturing process for disposable gloves is shown. Production proceeds with the ceramic former installed on the production line following a circular route around the drawing.

The compounded latex is constituted from latex and compounding chemicals.

Latex
The latices used in the dipping process are almost exclusively natural rubber (NR), polyisoprene rubber (IR), acrylonitrile butadiene rubber (NBR) and chloroprene rubber (CR). The word latex formerly indicated the white, milky sap collected from the rubber tree, but with the marketing of CR emulsion polymerisation products, the term also came to be applied to dispersions of fine

Table 1. Types of rubber glove

<table>
<thead>
<tr>
<th>Glove type</th>
<th>Textile support</th>
<th>Textile usage</th>
<th>Coverage of rubber</th>
<th>Thickness of rubber</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Yes</td>
<td>Liner</td>
<td>Whole surface</td>
<td>Thick</td>
</tr>
<tr>
<td></td>
<td>Yes</td>
<td>Liner</td>
<td>Palm only</td>
<td>Thick</td>
</tr>
<tr>
<td></td>
<td>Yes</td>
<td>Flock</td>
<td>Whole surface</td>
<td>Thick</td>
</tr>
<tr>
<td></td>
<td>No</td>
<td>-</td>
<td>Whole surface</td>
<td>Thick</td>
</tr>
<tr>
<td></td>
<td>No</td>
<td>-</td>
<td>Whole surface</td>
<td>Thin</td>
</tr>
</tbody>
</table>
rubber particles in a liquid consisting primarily of water. NR latex is an opalescent, viscous liquid secreted when the bark of the rubber tree is injured. It is an emulsion of rubber particles dispersed in aqueous solution as a colloid (particle size: 0.3-2.0 μm); as well as 35-50% of rubber, it contains small amounts of protein, resin, sugars, etc. The rubber particles are negatively charged and the disperse phase is positive.

On the other hand, latices of IR, NBR and CR, known collectively as synthetic rubber latices, consist of 0.1-1.0 μm polymer particles dispersed in water by virtue of a protective layer of surfactant, etc.

Synthetic latex is manufactured by emulsion polymerisation or polymer emulsification by means of mechanical shearing. The process may be batch polymerisation, semi-batch polymerisation, or seed polymerisation, in which the polymer composition, particle size, particle structure and shape are controlled. Other processes are soap-free polymerisation utilising the surfactant capacity of oligomer lightly polymerised with initiator present in the aqueous phase, and two-stage seed swelling polymerisation in which a seed latex is pre-swelled with an organic third component, thereby increasing the monomer content of the particles.

Compounding chemicals

Crosslinker
Colloidal sulphur is normally used with NR, IR and NBR latices. The range of usage is generally 0.5-2.5 phr (phr: ratio to parts by weight of rubber).

The crosslinker employed with CR and acid-modified NBR (XNBR), on the other hand, is zinc oxide, used in the range 4.0-5.0 phr for CR and 0.8-1.5 phr for XNBR.

Vulcanisation activator
JIS Type 2 zinc oxide and activated zinc oxide are used, the general range of usage being 0.5-2.5 phr. Zinc oxide is required for CR not only as a crosslinker but also to improve the age resistance of the vulcanised rubber by acting as a scavenger for chlorine liberated from the polymer.
Anti-ageing additive
In general, non-staining phenolic additives are much used.

PREPARATIONS BEFORE RUBBER GLOVE MANUFACTURE

Preparation of liquid dispersion
Compounding chemicals insoluble in water are made into an aqueous dispersion before being added to the latex. Dispersions of compounding chemicals are commonly prepared with the aid of a ball mill.

Preparation of compounded latex
The solids concentration and pH of the latex are first adjusted. The alkali used to adjust latex pH is generally ammonia or potassium hydroxide. Once preparation of the latex is complete, the various compounding chemicals are added. If a thickener is used, it is added last to bring the compounded latex to the desired viscosity.

Ripening of the compounded latex
The character of the compounded latex, and the physical or chemical properties of the gel film, dry film and cured film, vary with the storage temperature and time in storage. The effect depends on the kind of latex starting material and compound recipe, and is attributed to the changes that occur when dispersed particles of compounding chemicals and particles of emulsified oil disperse in the latex and are adsorbed on and permeate into the rubber particles, and to reactions in the latex (prevulcanisation of the rubber particles when vulcanising agents are incorporated) [2]. The ripening process is key to obtaining optimum product processability and maximum physical and chemical performance from a given formulation.

RUBBER GLOVE MANUFACTURING PROCESS

Direct dipping
Direct dipping is the simplest of the dipping processes: the specified former is alternately dipped in the compounded latex and dried until the desired product thickness is obtained. Vulcanisation is sometimes completed by drying on the former, but in other cases vulcanisation is conducted after stripping from the former. To hold the film thickness uniform and obtain constant physical properties, it is important to control the compounded latex solid concentration, pH, viscosity, thermal stability and temperature, the surface roughness and temperature of the former, and the speed at which the former is lifted, all of which have an effect.

Coagulant dipping
Most rubber gloves are fabricated by coagulant dipping. The film-forming mechanism exploits destabilisation of the latex by a coagulant (a polyvalent metal salt, organic acid or organic acid salt). Coagulant dipping is further divided into the anode process and Teague process.

The anode process entails dipping the former in the coagulant solution to deposit coagulant on the former surface and then dipping in compounded latex. The former is immersed in the latex for a set time until the specified thickness is obtained and then lifted out; the coagulated film formed on the former is washed with warm water and passed to the vulcanising step.

The process can accommodate film production over a very wide thickness range of 0.05-2.0 mm and has the further merit of affording uniform film of intricate shape. When gloves are manufactured by direct dipping, the finger crotch can become extremely thin owing to the surface tension of the latex, and gloves of the ultrathin type with a thickness of less than 0.1 mm are therefore manufactured by coagulant dipping.

Among the polyvalent metal salt coagulants used in the anode process, the most suited to dipping are calcium salts, of which calcium nitrate or calcium chloride are commonly used. The reason for this is the strength of the coagulant action and the homogeneity of the gel. The organic acid or organic acid salts used as coagulants are acetic acid and the cyclohexylamine salt of acetic acid.

Water, methanol, ethanol, etc., are used as solvents for dissolving the coagulant. To deposit the coagulant uniformly on the glove former, a little nonionic surfactant and calcium carbonate or calcium stearate, which have the effect of preventing adhesion to the skin, are added to the coagulant solution.

To produce supported latex gloves with a woven fabric liner, the former fitted with a glove of the woven fabric is first dipped in dilute coagulant solution (a methanol solution of a calcium salt) before being dipped in the compounded latex, the aim being to prevent latex bleeding through to the underside of the fabric. To meet this aim, the compounded latex has to be raised to a high viscosity with thickener.

The Teague process, on the other hand, operates in the opposite manner to the anode process: the former is dipped in the compounded latex and then immediately dipped in coagulant solution to effect gelation.
An example of its application is the manufacture of palm coated gloves, a type of supported latex glove. The glove former fitted with a woven fabric glove is dipped first in the compounded latex and then in a dilute coagulant solution to effect gelation; at the drying stage, fine porosity develops in the coagulated film as the methanol volatilises, conferring gas permeability.

Another process, multiple dipping, combines the anode and Teague processes, repeating them a suitable number of times.

**Heat sensitive dipping**

The former pre-heated to 40-60°C is dipped in compounded latex containing a heat-sensitive coagulant and left immersed for a specified time to obtain the prescribed thickness. It is important to control the stability of the compounded latex, the amount of stabiliser added, the pH of the compounded latex and the temperature, all of which affect the coagulant sensitivity to heat.

The heat sensitisers used include polyvinyl methyl ether and organopolysiloxane with a cloud point in the region of 30-50°C.

**Extraction step**

The water-soluble substances remaining in the coagulated film from dipping in compounded latex are generally undesirable. For example, the surfactants used for the stabiliser and dispersant have hygroscopic properties, while calcium salts and other coagulants will bloom out as time passes and are themselves quite hygroscopic. Moreover, the water-soluble proteins found in NR latex are a cause of immediate (type I) hypersensitivity and must therefore be completely extracted.

The timing of extraction in direct dipping is generally directly after evaporation of water by drying; in coagulant dipping the extraction is generally done directly after gelation following coagulant deposition. Extraction is by immersing the film in warm water. If the water is at too high a temperature, the film will shrink; a water temperature of 40-60°C is therefore preferred. The duration of immersion in warm water is of the order of 1-10 min depending on the film thickness.

The extraction of NR latex film in dilute aqueous alkali solution, for example aqueous ammonia or aqueous potassium hydroxide solution, promotes the removal of protein and is therefore effective in preventing type I hypersensitivity.

**Vulcanisation**

The usual method of vulcanisation is by hot air circulation blower. The minimum temperature for vulcanisation varies with the compounded latex. It is normally 90-100°C for NR and IR, 120-140°C for NBR, and 120-130°C for CR.

**Surface treatment**

To facilitate release from the hand former, to prevent gloves adhering to one another, and to ensure the gloves fit smoothly, gloves may be dusted, treated by chlorination, or given a polymer coating.

Dusting makes use of talc, silica, crosslinked starch, etc.

Chlorination treatment is carried out by dipping the gloves in chlorine solution. Reaction with chlorine creates a very thin layer of chlorinated rubber on the glove surface, thereby preventing tack. The chlorine solution is generated by directly injecting chlorine gas into water or by reacting hydrochloric acid with sodium hypochlorite. In either case, to preclude deterioration in anti-ageing properties, the glove surface must be neutralised with dilute alkali solution after reaction and then thoroughly washed. Temperature control in the subsequent drying step is also important since the film readily discolours if the temperature is too high.

A widely practised treatment for polymer coating is to dip the gloves in an acrylic or polyurethane type aqueous dispersion diluted to the requisite concentration.

**MARKET TRENDS IN RUBBER GLOVES**

Although the pattern of demand for rubber gloves varies with the product item, continued growth in demand may be foreseen against a background of increasing hygiene and safety consciousness among consumers.

The following major shifts in demand for disposable gloves have been seen in recent years.

* Shift in demand from NR gloves to synthetic rubber gloves
  - The switch from NR to synthetic rubber has been particularly evident in medical gloves. The aim has been to avoid the risk of type I hypersensitivity associated with NR. The actual changes are as follows:
    - Surgical gloves: There has been a switch from NR to CR or IR gloves.
    - Gloves for medical examination, investigation and diagnosis: There has been a switch from NR to NBR gloves.

* NBR gloves of thinner gauge
  - The thickness of single-use NBR gloves for medical examination has been decreasing. The factors behind the move to a thinner gauge may be listed as:
    - Ease of working while wearing the gloves (the search for a sensation of touch closer to bare hands)
The rising cost of materials and higher wages of glove manufacturing operatives

A relaxation in the EN Standard specifications (the specification for force at break ($F_b$) was lowered from 9.0 N to 6.0 N in March 2009)

Table 2 lists the standard specifications of disposable NBR gloves for medical examination in Europe and USA, the chief consumers.

NBR gloves that meet both standards are currently under intensive development. The ASTM standard stipulates a minimum glove thickness, and the greatest problem faced by developers is how to meet the EN specification of $F_b \geq 6.0$ at the minimum thickness of 0.05 mm. There is therefore a need to develop a high strength NBR latex for application as the principal source material for NBR gloves.

<table>
<thead>
<tr>
<th>Standard</th>
<th>Standard No.</th>
<th>Width of parallel part of die cutter mm</th>
<th>Film thickness at palm mm</th>
<th>Before ageing</th>
<th>After ageing</th>
<th>Ageing conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>ASTM</td>
<td>D6319-10</td>
<td>6</td>
<td>≥0.05</td>
<td>≥14</td>
<td>≥500</td>
<td>166±2 hours at 70±2ºC or 22±0.3 hours at 100±2ºC 7 days at 70±2ºC</td>
</tr>
<tr>
<td>EN</td>
<td>En455-2:2009 + A2:2013</td>
<td>3</td>
<td>-</td>
<td>≥6.0</td>
<td>-</td>
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</tbody>
</table>

**CONCLUSIONS**

Diverse types of rubber glove have been developed to match different service environments and property requirements, and it must be conceded that, on the whole, the niche segregation of forms and materials of gloves is now complete. Although the trend to overall growth of the rubber glove market is set to be maintained, therefore, the big manufacturers of rubber gloves are locked in fierce worldwide competition. We may anticipate that the creation of fresh demand through the release of added value products will be keenly pursued.

**REFERENCES**
