Science and Technology

Leather Tanning
Ono Suparno, Dept. of Agroindustrial Technology, IPB University, Bogor

Leather making is one of the oldest crafts performed by humankind. Although there is world-wide trend to exploit alternative materials derived from other sources, leather still finds widespread use.

Tanning is the most important step in leather production. It is typically carried out in an aqueous environment in rotating drums. During tanning, collagen will fix the tanning agent to its reactive sites, as a result stopping the putrefaction phenomenon. Tanning can be classified into three groups: mineral tanning, vegetable tanning, and other organic tanning (aldehyde, quinone, oil, and synthetic tanning).

***

Mineral Tanning
Ono Suparno, Dept. of Agroindustrial Technology, IPB University, Bogor

Four elements play a significant role in the modern leather tanning industry, i.e. chromium(III), aluminium(III), titanium(IV), and zirconium(IV), of which chromium(III) is the most important. Nowadays, more than 90% of the world’s leather is tanned with chromium, which is a consequence of the easy processing, the broad achievability and the excellent properties of leather. Tanning using Cr(III) sulfate can achieve shrinkage temperatures above 120°C. However, it also has considerable potential for environmental pollution.

The interactions of collagen with chrome have been extensively investigated since the end of the nineteenth century. The fundamental reaction is the formation of complex bonds with the ionised carboxyl groups of aspartic and glutamic acid residues on collagen fibres.

Other mineral tannages (Al(III), Ti(IV), and Zr(IV)) have similar reaction mechanisms
to chromium, although reaction is dominated by electrovalent bonding, thus much lower shrinkage temperature is obtained than with chrome. The maximum shrinkage temperatures of leather tanned with Al(III), Ti(IV), and Zr(IV) salts are 79, 90, and 97°C respectively. The development of titanium and zirconium tannage is relatively new. Empirically, the chemistry of Ti(IV) is dominated by the titanyl ion \( \text{TiO}_2^+ \) and the species in the tanning agent are chains of \((\text{Ti-O})_n\). Zirconium salts are characterised by eight-coordination and high affinity for oxygen, resulting in a tetrameric core structure; the basic unit of structure is four Zr(IV) ions at the corners of a square. The tanning powers of titanium and zirconium are similar and both are better than aluminium.

***

**Oil Tanning**

Ono Suparno, Dept. of Agroindustrial Technology, IPB University, Bogor

Oil tanning is a very old way of imparting the properties of finished leather to skins. In modern oil tanning for chamois leather, the flesh split of the sheepskins are used as having desirable open fibre structure. After the usual beamhouse processes, they are brought to the isoelectric point, e.g. pH 4.5.

Penyamakan minyak adalah penyamakan kulit menggunakan minyak, biasanya minyak ikan, untuk menghasilkan kulit samak minyak (chamois leather). Metode tradisional pembuatan kulit chamois adalah mengimpregnasi kulit domba split basah dengan minyak ikan dalam fulling stocks dan kemudian menggantungnya dalam stoves hangat untuk oksidasi minyak.


***

Quinone Tanning

Ono Suparno, Dept. of Agroindustrial Technology, Bogor Agricultural University (IPB), Bogor.

Quinone tanning is usually separately discussed as a specific tanning process. The tanning agent involved is a compound of small molecular size, containing a functional group of one kind only. In the time of chromium shortage (e.g. in France during World War II), quinone was used in the pretanning process.

Quinones react with the collagen amino groups to form aminohydroquinone or 2,4-aminoquinone. As a result of nucleophilic attack on quinone, ring aromatisation occurs: the redox potential of quinone decreases by about 250 mV, so the compound obtained is easily oxidised by another quinone molecule; hence two hydroquinone molecules may react, so a cross-linking quinone is formed. Products of this type can be separated from the reaction mixture.

The reaction kinetics are pH-dependent; in acidic or alkaline (pH 10) medium, the Ts increases rapidly, then it maintains the level reached or drops slightly. In neutral solution, the Ts initially rises quickly, but the reaction remains incomplete for a long time.

Quinone tanning is conducted in buffer solution, because with pH increase, quinone solutions become dark and so does the leather. The properties of the anion of the
buffering compound affect the value of pH at which quinone-collagen binding occurs. For borate buffer, the optimal binding pH is about 5, for phosphate it is pH 7-8. The tanning process takes 24-48 hours.

The shrinkage temperature (Ts) of quinone tanned leathers may be as high as 90°C. The amount of quinone bound is high, 20% or more, particularly at optimal pH. The proteolytic resistance of quinone-tanned leather is very high.

***

**Vegetable Tanning**

Ono Suparno, Dept. of Agroindustrial Technology, Bogor Agricultural University (IPB), Bogor.

Vegetable tannins or natural polyphenols are complex higher plant secondary metabolites. They are water soluble, have relative molecular masses in the range 500-3000 and besides giving the usual phenolic reactions, they are able to precipitate some alkaloids, gelatine, and other solution from protein, from solution. They may be extracted from plant material containing polyphenols. They can be classified into three major groups: hydrolysable (pyrogallol), condensed (catechol), and complex tannins.

Hydrolysable tannins are sugar derivatives, based on glucose, but may be larger polysaccharides. Depending on the polyphenolic acids that are obtained as products of hydrolysis, hydrolysable tannins can further be divided into gallotannins (a) and ellagitannins (b) (Figure 1.3). Gallotannins yield gallic acid and glucose on hydrolysis. The ellagitannins produce ellagic acid in addition to gallic acid and glucose on hydrolysis. The hydrolysable tannins give good filling effect and typically raise the shrinkage temperature of collagen to 75-80°C. Commercially used hydrolysable tannins are listed in Table 1.1.

<p>| Table 1.1 | Commercially used hydrolysable tannins | 6,7 |</p>
<table>
<thead>
<tr>
<th>Tannin</th>
<th>Type of tannin</th>
<th>Plant</th>
<th>Part of the plant</th>
<th>Tannin content (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chinese tannins (tannic acid)</td>
<td>Gallotannin</td>
<td><em>Rhus semialata</em></td>
<td>Galls, leaves</td>
<td>34-71</td>
</tr>
<tr>
<td>Turkish tannin</td>
<td>Gallotannin</td>
<td><em>Quercus infectoria</em></td>
<td>Galls</td>
<td>25-45</td>
</tr>
<tr>
<td>Sumach</td>
<td>Gallotannin</td>
<td><em>Rhus coriaria, R. typhina</em></td>
<td>Leaves</td>
<td>26-27</td>
</tr>
<tr>
<td>Tara</td>
<td>Gallotannin</td>
<td><em>Caesalpinia spinosa</em></td>
<td>Fruit pods</td>
<td>45-59</td>
</tr>
</tbody>
</table>
Terminalia chebula
Quercus valonea
Condensed tannins are referred to as polyflavanols or proanthocyanidins; they are based on the flavonoid ring system (Figure 1.4)\textsuperscript{6,45}. The A ring usually contains one or two phenolic hydroxyl groups; the B ring, which typically has a catechol structure, has different reactivity\textsuperscript{45}. The fundamental structure of the tannins is the phenolic flavan-3-ol, present in catechin (cyanidin), gallocatechin (delphini-din), fisetinidol, and robinetinidol. The flavan-3-ol units are linked through the C-4 to C-8 positions and C-4 to C-6 positions. General structures of the condensed tannins are shown in Figure 1.5\textsuperscript{8,21,22,45}. Sources of condensed tannins are given in Table 1.2. They typically raise the shrinkage temperature of collagen to 80-85°C\textsuperscript{45}. 
Complex tannins are built up from a gallotannin unit or an ellagitannin unit and a catechin unit. One example of this group is acutissimin A, having a flavogallonyl (nonahydroxytriphenoyl) unit bound glucosidically to C-1, and linked via three further hydrolysable ester bridges to the D-glucose derived polyol.

Vegetable tannins react with collagen primarily via hydrogen bonding, as demonstrated in the model in Figure 1.6. Hydrophobic interactions have also an important role, particularly in hydrolysable tannins. Condensed tannins are more resistant to removal by hydrogen bond breakers because they have an additional mechanism for reaction, which is covalent reaction between the protein and aromatic carbon in tannin molecules via quinoid structures. Quinone itself can tan collagen effectively.
Table 1.2 Sources of condensed tannins

<table>
<thead>
<tr>
<th>Family</th>
<th>Plant</th>
<th>Part of the plant</th>
<th>Tannin content (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Myrtaceae</td>
<td><em>Myrtan</em> / <em>Eucalyptus</em></td>
<td><em>Eucalyptus astringens</em></td>
<td>Heartwood</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><em>Eucalyptus wandoo</em></td>
<td>Bark</td>
<td>12-15</td>
<td></td>
</tr>
<tr>
<td>Leguminosae (Wattle/mimosa)</td>
<td><em>Acacia mollisima</em></td>
<td>Bark</td>
<td>35-40</td>
</tr>
<tr>
<td><em>Acacia catechu</em></td>
<td>Heartwood</td>
<td>15</td>
<td></td>
</tr>
</tbody>
</table>
Robinia pseudacacia
Schinopsis
balansae
Rhizophoraceae (Mangrove)
<table>
<thead>
<tr>
<th>Fagaceae</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>(Oak)</td>
<td></td>
</tr>
</tbody>
</table>
Quercus robur
Pinus sylvestris
| Larix decidua |  |  |
Rubiaceae
(Gambier)
What is lignin?
Ono Suparno, Dept. of Agroindustrial Technology, IPB University, Bogor

Lignin is a major component of vascular tissues in terrestrial plants: it is an amorphous, water-insoluble, three-dimensional aromatic polymer. It is found in higher plants, including ferns, but not in liverworts, mosses, or plants of lower taxonomic ranking. Wood and other vascular tissues generally contain 20-30% lignin, mostly found within the cell wall, where it is intimately interspersed with the hemicelluloses, forming a matrix that surrounds the orderly cellulose microfibrils. In wood, lignin in high concentration is the glue that binds contiguous cells, forming the middle lamella.

Lignin is the material that confers the qualities of rigidity and durability of wood. In this natural composite material, the cellulose fibrils provide tensile strength, and the hemicellulose and lignin provide cross-linking, binding the structure together.

Biosynthesis of lignin

Lignin is derived from phenylalanine and, in grasses such as bamboo and wheat, from both phenylalanine and tyrosine, which are synthesised from sugars via the shikimic acid pathway. Figure 1.12 shows the pathways in the biosynthesis of lignin from carbon dioxide. L-phenylalanine is converted to trans-cinnamic acid, catalysed by phenylalanine ammonia-lyase (PAL), which is a key enzyme in the synthesises of various phenolic compounds including lignin and is widely distributed in higher plants. Tyrosine ammonia-lyase (TAL), which catalyses the formation of p-coumaric acid from tyrosine, is characteristically found in grasses, the lignin of
which contains p-coumaryl alcohol as an additional lignin monomer as well as esterified p-coumaric acid. Deamination, ring hydroxylation, phenolic methylation, and carboxyl reduction steps lead to the intermediate cinnamyl alcohol precursors of lignin, i.e. p-coumaryl, coniferyl, and sinapyl alcohols. Figure 1.13 illustrates the chemical structures of lignin precursors.

Lignin is made by the oxidative polymerisation of the cinnamyl alcohol precursors. Single electron oxidation of the phenolic hydroxyls in these precursors within the lignifying cell wall produces radical species, which exist in mesomeric forms. These couple essentially randomly with each other, but primarily with radicals in the growing lignin polymer, which contains phenolic hydroxyls and is itself a substrate for single electron oxidation. Figure 1.14 illustrates various structural features in a schematic formula of aspen lignin.

Synthesis of a polymer resembling lignin can be achieved by oxidative polymerisation of coniferyl, sinapyl, and/or p-coumaryl alcohol using commercially available horseradish peroxidase and hydrogen peroxidase. This synthetic lignin or dehydropolymerisate (DHP) of coniferyl alcohol is a macromolecular material and contains an inter lignol bond identical to those found in native lignin.

**Biological degradation of lignin**

Lignin is biodegraded by a unique enzymatic ‘combustion’, i.e. non-specific enzyme-catalysed mineralisation. Lignin is degraded by a narrower array of microorganisms than the other major biopolymer, cellulose. Lignin biodegradation is central to the earth’s carbon cycle because lignin is second only to cellulose in abundance and perhaps is more significant, because lignin physically protects most of the world’s cellulose and hemicellulose from enzymatic hydrolysis.

Due to the size, non-hydrolysability, heterogeneity, and molecular complexity of lignin, its initial biodegradation is oxidative and non-specific, and mediated by an extracellular system. It is clear from observation of lignin mineralisation that its conversion to CO₂ and H₂O is thermodynamically favoured.