Going Green:

Using non-toxic catechin to treat denaturation in leather and skin materials

Mari Hagemeyer
Andrew W. Mellon Fellow, The Walters Art Museum · mehagem@gmail.com

The skin you're in

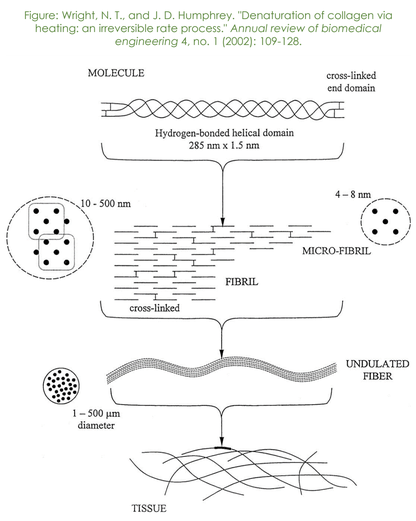


Figure: Wright, N. T., and J. D. Humphrey. "Denaturation of collagen via heating: an irreversible rate process." *Annual review of biomedical engineering* 4, no. 1 (2002): 109-128.

Skin is a fibrous material largely made up of **collagen**, a flexible protein found in the organs as well as in hair, muscle, and bone. In its natural state, skin has a **multilayer structure** with a significant amount of water adsorbed to the material. This **structure is preserved** in leather and skin materials, albeit in a transformed way.

In rawhide, which is **not chemically processed** in any way, the fibrous layers of the skin **collapse** when dried and **swell** when wet; other kinds of chemical processing such as tanning **restrict** this swelling behavior by **cross-linking the chains** or by **replacing the water** with another material, such as oil.

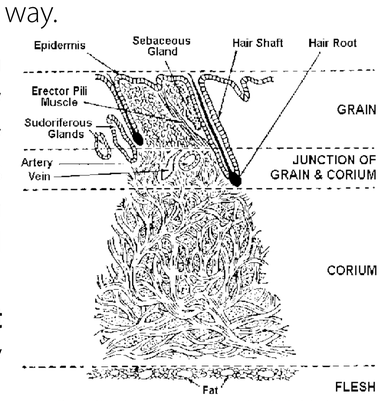


Figure: Sharphouse, John Henry. *Leather technician's handbook*. Leather Producers' Association, 1983.

Water, water everywhere

As a proteinaceous material, collagen is very **sensitive to water**. If too much water is available to the system, it begins to **disrupt the structure** of the material and turn it into a **disordered gel**, which dries to a **glassy solid**. This process is known as **denaturation**.

Denaturation is one of several major deteriorative paths that affects leather. Leather may:

- **Decay** biologically
- Undergo "**red-rot**"
- Become **waterlogged**
- Or **denature.**

Denaturation is most common in **untanned and semi-tanned** skin materials, which are more susceptible to water. Red-rot is common in historic **book bindings**, while most most **archaeological leather** is waterlogged and/or partially decayed.

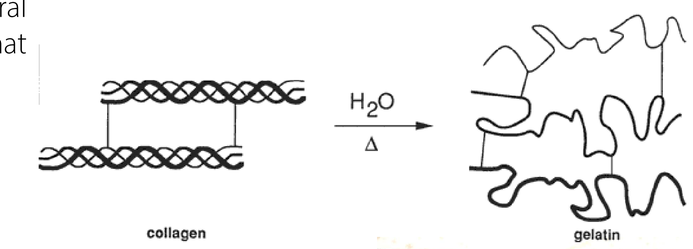
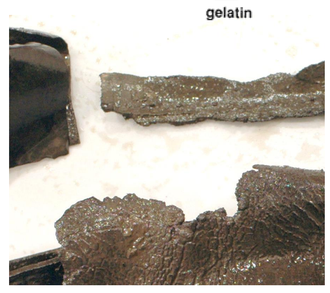


Figure (above): Scott, J. "Molecules that keep you in shape." *New Scientist* 111, no. 1518 (1986): 49.

Red-rotted leather book binding



Waterlogged archaeological leather shoe

The problem is, there is no treatment in current use to address the effects of denaturation on collagenic materials, especially embrittlement.

Make a matcha marinade

An experiment was devised to compare the effect of a **novel treatment**, targeted at denaturation damage, to the effects of **other treatments**, which were developed for waterlogged organic materials. This novel treatment was chosen for its demonstrated ability to **reduce water sensitivity** in collagen by **cross-linking the chains**. In all, **three treatment materials** were tested:

Polyethylene glycol (PEG)

PEG is an **organic consolidant** typically used for waterlogged wood and leather. Shorter-chain PEG 400 is preferred for leather. PEG **does not react** with the treated material and is **somewhat reversible**.

Silicone coating (Dow 1248 fluid)

Silicones are **inorganic polymers** based on silicon dioxide, which **react with or within** the treated material to create an interpolating structure. They are controversial due to their **irreversibility and non-retreatability.**

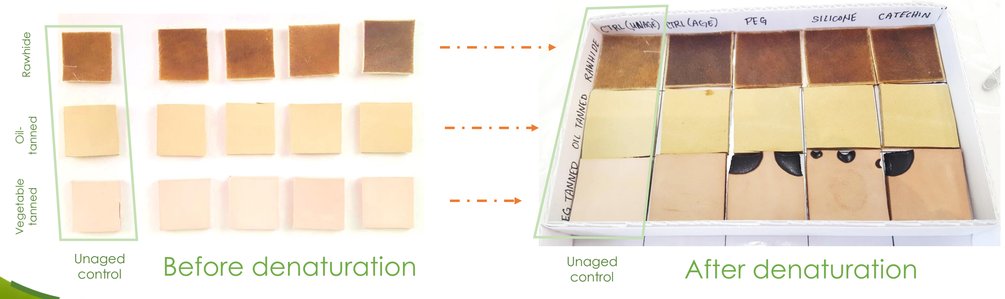
Catechin (EtOH solution)

Catechin is a **flavonoid** found in **green tea**, among other sources. It reacts with collagen in a **similar way to tannins**, creating crosslinks between collagen fibrils, and is **retreatable, but not reversible.**

Experimental layout:

Coupons were cut from **vegetable-tanned leather**, **oil-tanned leather**, and **rawhide**, then kept in an oven at 80°C and 80% RH for 15 days to **artificially denature** them. Samples were also taken from a **brain-tanned leather** armband, which had already become **partially denatured**.

All these samples were then treated with **one of the three treatment materials**. **PEG** was applied in a solution with ethanol, which was then evaporated off; **Dow 1248 fluid** was applied by brush; and the **catechin solution** was applied in a cellulose poultice. After treatment, the coupons were **investigated with DSC** (differential scanning calorimetry)**, FTIR, and FORS**.

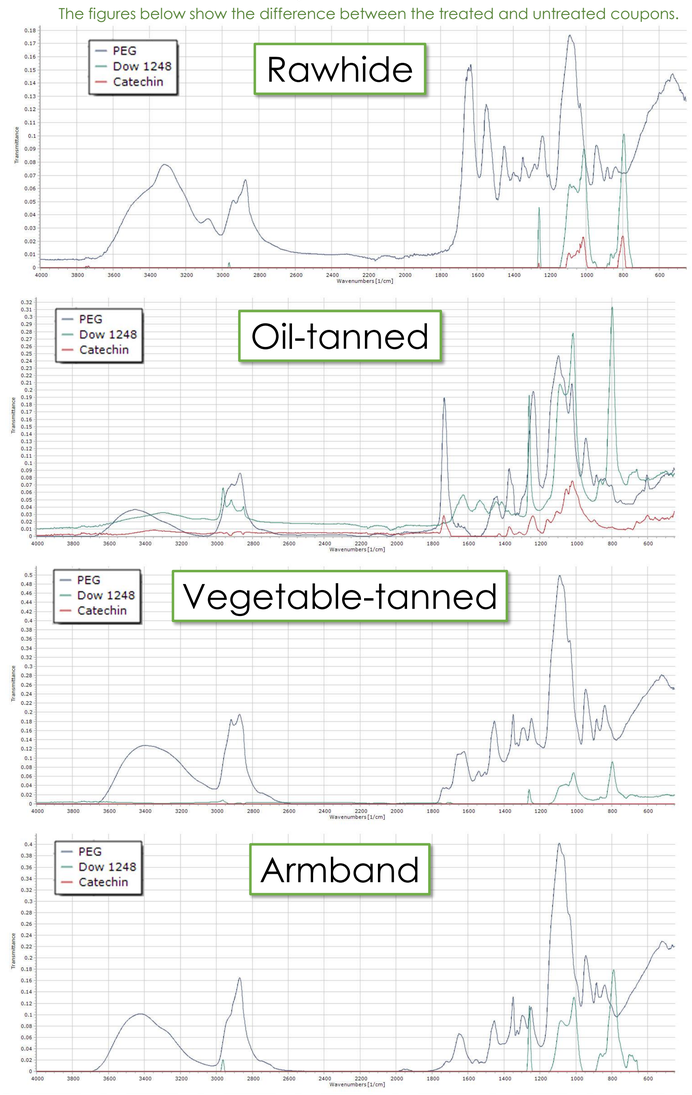


Putting tea to the test

The samples were assessed with two questions in mind: **how much** did they change, and **in what way**? Chemically, the **least possible change** was desired, while physically, an **increase in water resistance** was needed. These properties translate closely to two analyses: FTIR data describe the material's **chemical properties**, while DSC data describe the material's **sensitivity to water and heat**.

DSC data	PEG treatment		Dow 1248 treatment		Catechin treatment	
Tannage	**T_s**	**W_p**	**T_s**	**W_p**	**T_s**	**W_p**
Rawhide	∅	∅	↓	↔	∅	→←
Oil-tanned	↓	→←	↓	∅	↑	→←
Vegetable	∅	∅	∅	∅	∅	∅
Armband	∅	→←	∅	→←	↓	→←

The figures below show the difference between the treated and untreated coupons.



The table above summarizes the DSC findings. T_s indicates **shrinkage temperature**, which is inversely related to water sensitivity. The **higher the T_s**, the **lower the water sensitivity**. W_p indicates **peak width**, which describes **how uniform the material's response** to water is.

Although these results were somewhat contradictory, there are a few clear trends. PEG caused **little to no change** in the material; silicone caused **mostly negative change** in the material; and catechin caused **mostly positive changes**.

FTIR data were **transformed in several ways** to show variations in chemical makeup. The spectra from treated samples were **subtracted from the control spectrum** for each material, and then compared with one another. Again, there are several distinct trends that develop: **PEG caused the most** material change, while **catechin caused the least.**

Know how to treat them right

Leather armband after treatment with catechin solution

Although more research needs to be done before catechin can be used as a treatment, this experiment has very **promising results**. It establishes three points:

- Leather treatments in current use are **not effective** in treating denaturation.
- Of the treatments tested, catechin caused the **least chemical change** in the material.
- Of the treatments tested, catechin caused the **most positive change** in water sensitivity.

In addition to these quantifiable data, there were also qualitative changes in materials treated with catechin, such as **increased flexibility**. Hopefully, future research will be able to quantitatively test this property, so the effects of catechin may be better understood.

Coupons after treatment with tested materials