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Animal Glues – their adhesive properties, longevity and suggested use for repairing taxidermy specimens

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Introduction
Animal glues have a long tradition of being used as structural adhesives, sizes and consolidants not only in furniture making but also in the preparation and conservation of the most varied materials such as those found in natural history collections. With a variety of different animal glues on the market, such as hide and bone glues, fish glues, isinglass and gelatin, their individual properties need to be well understood in order to determine whether and which of these glues are appropriate for a specific purpose. This paper will look at some of the most important physical, chemical and mechanical properties of collagen-derived glues, their stability and ageing properties (a list of which can be seen in Appendix 1), and will consider their appropriate use in taxidermy conservation.[1]

Chemical structure and properties of animal glues

Chemical structure and denaturation
Animal glues are natural polymers derived from mammalian or fish collagen – the major structural protein constituent of skins, connective tissue, cartilage and bones. Collagen consists of long protein molecules composed of naturally occurring amino acids that are linked in specific sequence by strong covalent bonds. Due to the spatial structure of some amino acid units and the presence of many ionisable and polar functional groups in the protein molecule, the individual chains form triple-stranded helical coils (Fig 1) that are internally stabilised by hydrogen-bonding (Woodhead-Galloway, 1980).

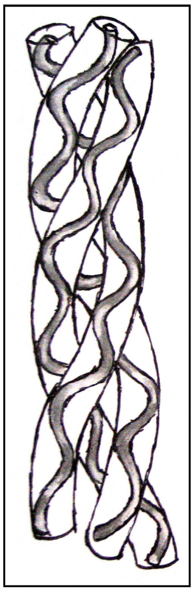

Fig 1. Collagen triple-helix

Collagen itself is insoluble in cold water, and its transformation into soluble gelatin is of critical importance for the performance of the resulting glue. The transition (a process known as *denaturation*) is achieved by pre-treating the raw collagen with acids or bases followed by hot water extraction. During this process, the stabilising bonds (predominantly hydrogen-bonds) are broken which causes the triple-helix formation of the collagen molecules to separate into disordered coils of single protein chains, of which gelatin is composed (Rivers and Umney, 2003). The temperature (T_d) at which collagen denatures is typical for its source and is dependent on the chemical structure of the proteins. Generally, mammalian collagen has higher T_d at around 40-41°C compared with that of marine species, which converts to gelatin at much lower temperatures (Holmgren, 1998). Collagen of deep, cold water fish (such as cod used for fish glue) denatures at approximately 15°C while warm water species, which are the preferred source of isinglass produced for commercial clarification of alcoholic beverages, have a T_d of up to 29°C (Haug et al, 2004, Norlands product).

Denatured collagen in its pure form is pure gelatin. However, unless the denatured collagen is purified, the gelatin-based glue matrix gained after extraction contains many impurities, e.g. other protein degradation products, minerals and fats. Glues such as hide and bone glue, rabbit skin glue or cold-liquid fish glue contain many impurities and thus have a yellow or brown colour. Bovine or porcine gelatin, available in food stores or from chemical suppliers, is the purified product. Isinglass, usually extracted directly by the end user from commercially available dried fish bladders, is naturally a very pure product. This is because fish bladders are the source containing the highest amount of collagen, which is also the least chemically linked, and thus only requires the mildest extraction procedure.

Gelation and gel strength
Gelatin in solution has the ability to form a rigid gel upon cooling, which can be repeatedly reactivated with heat. Gelation is based on the partial rearrangement of the protein solution's single random coils back into collagen-like triple helices, occurring at around 32ºC in mammalian gelatin and at temperatures as low as

around 8 ºC in cold water fish gelatine (Horman and Schlebuschm 1971, Haug et al, 2004, Badii and Howell, 2006). This renaturation only develops in sections due to natural misalignment of the single strands, and a continuous three-dimensional network structure is formed (Fig.2a-b). The number of nodes that are established by hydrogen-bonds within and between the molecules determines the rigidity and elasticity of the gelatin or glue matrix, and is measured as gel strength (also known as Bloom strength) (Kozlov and Burdygina, 1983).

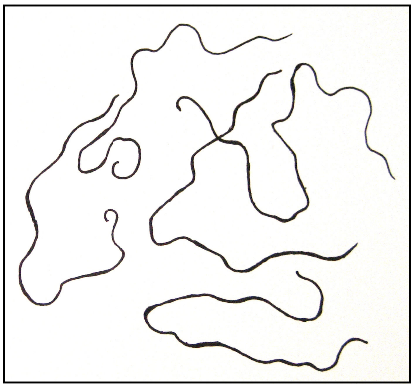

Fig 2a. Denatured collagen, consisting of individual protein strands

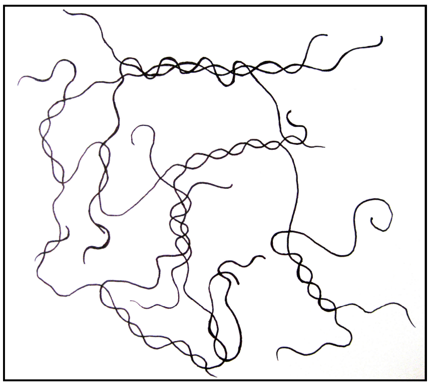

Fig 2b. Renaturation of protein strands (gelation)

Gel strength is strongly influenced by the molecular weight of the protein molecules, but is also determined by the polymer's chemical composition (which varies with the collagen source and is also influenced during manufacture), and its concentration in solution and temperature, which affects the renaturation level (Kozlov and Burdygina, 1983, Horman and Schlebuschm 1971). Long protein chains, high solution concentrations and slow gelation at low temperatures promote the development of collagen-like helical formations and highly ordered network structures that produce high gel strength (Hickman *et al*, 2000, Hull and Bangert, 1952). Mammalian gelatine produces higher gel strengths than that of marine species.

Molecular weight

The molecular weight of the protein chains is one of the most important properties of gelatin-based glue as it influences many of its adhesive properties. Generally, the more vigorous the extraction process of the glue during manufacture (i.e. the more extreme the pH during pre-treatment, the longer the treatment and the higher the temperature at extraction), the more the long protein chains are broken down, which leads to increasingly lower molecular weights (Hickman *et al*, 2000). Mild extraction at moderate pH and low temperatures yields gelatin-based glues with long chain lengths and high molecular weight (MW) (Hull and Bangert, 1952, Haupt, 2004). As a general rule, gentle processing is appropriate for the hides of young mammals, fish skin and swim bladders because they are rich in collagen content and less stabilised by additional chemical bonds that develop in collagen with ageing. Preparation of animal glues prior to their use by conservators should also follow mild procedures (Luybavskaya, 1990, Haupt, 2004). Ideally, gelatin-based glue solutions should always be prepared fresh and not be kept heated for longer periods, as the glues will gradually degrade and lose their adhesive properties. It is generally recommended to prepare glue solutions at around 60°C, but it should be noted that heating at elevated temperatures (e.g. 80-90°C) can take place without much loss of gelling power if such temperatures are limited to a few minutes only (Haupt, 2004).

Animal glues can be characterised by their average molecular weight to roughly indicate the physical and mechanical properties of the adhesive such as gel strength, viscosity, penetration ability, speed of set and final bond strength. For example, high average MW adhesives are usually expected to have higher gel strength, be more viscous, penetrate less, gel more rapidly and produce stronger bonds. A more common way of characterising gelatinous glues, however, is by giving their gel strength, which reflects their properties in use.

Influence of gel strength on physical and mechanical properties

The cohesive strength of a gelatine-based glue is determined by its molecular structure and intermolecular bonding, as expressed in Bloom values. To produce strong animal glue films with great stiffness and a high resistance to impact in the dried state, the same rules apply as obtaining high gel strength, i.e. long protein molecules / minimum degradation, high content of renatured collagen-like triple-helices, and high intra-/ intermolecular bonding. Hide glues generally have greater cohesive strength than strongly denatured and degraded bone glues, which display lower tensile strength and are much more brittle. Mammalian collagen tends to yield stronger glues than most aquatic sources, owing to reduced contents of stabilising inter- and intramolecular bonds in fish collagen (Hormann and Schlebusch, 1971). Cold water fish gelatin in particular shows comparatively low tensile strength which is comparable with that of bovine bone gelatine, while a high tensile strength, similar to that of hide glue, has been reported for mildly prepared sturgeon isinglass (Luybavskaya, 1990, Simon et al, 2003, Zumbuhl, 2003).

Stability with ageing and resolubility

Dry conditions cause gelatine-based glues to dry out, shrink and embrittle, due to the development of high inner stress and tensile forces within the glue matrix. In conditions of changing relative humidity (RH,) low gel strength glue will deteriorate rapidly in their mechanical properties, while high gel strength glues retain their mechanical properties much better. The reason for this is because at high RH levels a continuous renaturation of the protein molecules is taking place which increases the stress in the glue matrix upon drying. Due to their more elastic molecular structure, highly renatured glues can compensate inner stresses much more successfully than low gel strength glues.

Of all animal glues, sturgeon isinglass best retains its mechanical properties with ageing, closely followed by mammalian gelatine, as it remains much tougher and more elastic as well as showing less dimensional changes than any other gelatine-based glues (Michel *et al*, 2002).

Generally, animal glue readily swells in water and shows good resolubility even after centuries, unless it has developed strong internal cross-linking of the protein molecules. This happens when the glue is either deliberately treated or accidentally exposed to metal salts, formaldehyde or other tanning agents. Particularly, ready-made liquid hide and fish glues may contain unknown additives that promote cross-linking which will render the glues increasingly insoluble.

Considerations for the use of animal glues in taxidermy conservation

When it comes to choosing an appropriate adhesive for the conservation of taxidermy specimen, certain requirements are of particular interest. The adhesive should :

- have appropriate adhesion and cohesion properties
- minimally interfere with the original skin material
- be reversible or at least render the specimen retreatable
- be stable with ageing

Adhesion and cohesion properties

Considering that gelatinous glues are a chemical derivative of collagen, they can generally be considered a suitable type of adhesive for skins and other collagen-based products, as they are able to develop good chemical adhesion to the substrate. Gelatin-based glues containing long protein chains (i.e. having high gel strength such as hide glue or isinglass) also show very strong cohesion and would thus be an appropriate choice.

Interference with original skin material

Sensitivity to moisture:

Animal glues are very sensitive to changes in relative humidity, as are taxidermy specimen, and they will subsequently react with dimensional changes. This, however, may not be desirable for the conservation of taxidermy specimen, and it may be considered more appropriate to opt for an adhesive that is less sensitive to moisture. As gelatin-based glues are applied in an aqueous solution, the water sensitivity of the specimen has to be considered, too. Low viscosity glue solutions and those which gel slowly (such as isinglass) are problematic in cases where the substrate is very water sensitive. Fast-gelling glue solutions (those with a high gelling temperature) would be a more suitable choice in such cases, or even the use of a non-aqueous adhesive.

Denaturation temperature (T_d) of specimen:

The collagen material in some taxidermy specimen may have a very low denaturation temperature, e.g. fish and reptile skins or strongly degraded skins of other animals. Using hot hide or bone glue on such a specimen would risk the denaturation of its collagen, while cold-liquid fish glue or isinglass could be applied with much less risk of damaging the specimen.

Colour:
For light coloured or semi-transparent specimen only high gel strength gelatin or isinglass should be considered, as all other animal glues have a yellow to brown colour and low gel strength gelatin has the tendency to yellow with age.

Reversibility and stability with age
The original preparation treatment of the taxidermy specimen may have an influence and long-term effect on a gelatin-based glue that is applied to it. If the specimen had been prepared using metal salts or other tanning agents, which still remain in the substrate, these can react with the gelatin and cause it to develop strong chemical crosslinking that will render the glue increasingly insoluble in water.

Conclusion

Gelatin-based glues may under certain circumstances be a suitable type of adhesive for the conservation of taxidermy specimen. In many cases, however, their application in an aqueous solution as well as their great sensitivity to moisture with stress development in fluctuating environmental conditions may cause an array of unwanted interactions with the specimen. Last but not least, their chemical affinity to skin material and their potential to contaminate the original DNA of the taxidermy specimen has to be acknowledged so that the use of gelatin-based glue should thus always be weighed up against the advantages of alternative synthetic adhesives.

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Notes
[1] This article is based on a presentation given at the NatSCA Seminar on Adhesives for Natural Science Specimen held at the NHM on 18. 11.2008. The paragraphs about the chemical, physical and mechanical properties of animal glues are an abbreviated summary of the article ‘Animal glues: a review of their key properties relevant to conservation’ originally published by N. Schellmann in *Reviews in Conservation* **8** (2007), pp.55-66.

Appendix 1.
Table of animal glues and their properties.

PROPERTY / GLUE TYPES	molecular weight (MW)	gel / Bloom strength [gB]	viscosity	mechanical strength	elasticity	stress development in fluctuating RH	stability in fluctuating environment
Property dependency	decreases with rigorous pretreatment and with excessive / prolongued heating	increases with higher MW and increasing content of helical structures	increases with increasing Bloom strength	increases with increasing content of helical structures	increases with increasing molecular weight, helicity and solution concentration	increases with increasing content of helical structures	increases with increasing content of helical structures
bone glue	low to medium	low to medium	low to medium	low to medium	more elastic than hide glue (but more brittle, too)	medium	less stable than hide / rabbit skin glue
hide glue	high	high	medium to very high	medium to high	less elastic (stiffer) than bone glue, and gelatin from aquatic sources	high	more stable than bone glue
rabbit skin glue	high	high	high to very high	high	more elastic than hide glue	high	less sensitive to moisture than hide glue
mammalian gelatin	medium to high (pure gelatin is produced with different average molecular weight)	high	medium to high	medium to high	less elastic (stiffer) than gelatin from aquatic sources	medium to high	less stable than isinglass
isinglass (from fish swim bladders)	high to highest	medium to high	very high to highest	high	more elastic than hide glue	very high	higher than mammalian gelatin
liquid fish glue	low	-	high (at manufactured concentration)	medium	more elastic than hide glue (but more brittle, too)	medium	less stable than cold liquid hide glue