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The mechanical properties of composites manufactured from tendon fibres and pearl glue (animal glue)

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Abstract

The mechanical properties of a composite manufactured from bovine tendon and pearl glue (an animal glue containing gelatine and other proteins) are investigated. This composite was traditionally used in the construction of Asiatic re-curve bows for archery and is reputed to be tough yet elastic. Composites were manufactured by hand laying fibres into a mould and then pouring on hot glue. Tensile tests were performed on the specimens with the load being applied along the long axis of the fibres. The composite was found to absorb 18 MJ/m^3 of energy to failure, comparable to carbon fibre composites, spring steel and butyl rubber. This energy absorption was achieved through the ductility and strength of the collagen fibres, which were found to be several times larger than the glue (fibre strength was 180 MPa, glue strength was 32 MPa, fibre failure strain was 26%, glue failure strain was 3%). However, the tensile modulus of the fibres and glue were similar. The composite was also found to be extremely damage tolerant, with many micro-cracks developing between strains of 2–20%, and dominated by elastic behaviour to surprisingly large deformations. The reasons for this are discussed.

Keywords: A. Glass fibres; A. Resins; B. Debonding; B. Fracture; Natural fibre composite

1. Introduction

Predictions of global warming have lead governments to try to encourage the use of sustainable resources, reduce our dependence on fossil fuel based technologies and increase our efficiency of material use. Focusing on the sectors of structural materials and engineering composites it has been realised that natural materials can offer advantages over synthetics in terms of energy efficiency, cost and re-cyclability. In this context, there has been a large amount of work to find natural alternatives for glass fibre-reinforce plastic (GRP). Plant fibres such as hemp and sisal have been used to replace the glass fibre, while plant oils such as cashew nut liquid have been used to make plastic replacements [1–4]. This work has been very successful and a number of large car manufacturers currently use the technology to produce internal vehicle mouldings. However, natural fibre-reinforced plastics have not replaced GRP in structural applications, where higher performance is required, because their mechanical properties, such as toughness and strength are generally inferior.

To date there has been very little research looking at using animal derived natural materials in high performance composite applications, with the obvious exceptions of silk [5] and the possible exception of some prosthetic materials in the medical industry [6]. This is despite the fact that animal fibre composites have been used for thousands of years in high performance structures such as the archery bow. Archery has played an important role in the development of human civilisations and some of the weapons that were being manufactured thousands of years ago were extremely sophisticated combinations of different natural materials. One of the best examples is the Asiatic re-curve bow (of which there are many variations), made from a laminate construction, with a wooden core, backed by tendon on one side and horn on the other [7]. The tendon lies on the tensile surface of the strung bow and the horn on the compressive side, with the wood acting as a spacing device. This combination of materials was designed to store large amounts of elastic strain energy when the bow was strung and pulled. What is of particular interest for this paper is the tendon layer.

The tendon layer is a composite of tendon and animal

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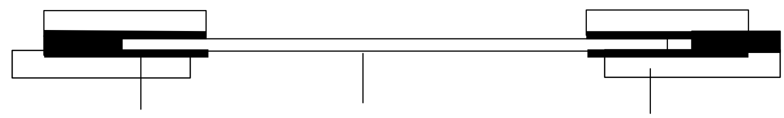

Fig. 1. Diagram showing the metal tabs that were glued onto the ends of the tensile specimens to prevent the ends being crushed during clamping.

glue (gelatine and other proteins), dried to form a hard material and reputed to be extremely resistant to tensile failure and capable of storing large amounts of strain energy. The fibres and matrix of the tendon layer are highly compatible because they are made from the same molecular components, i.e. collagen. The difference is that the fibres are made from highly ordered collagen while the matrix consists of disordered (denatured) collagen (gelatine) and other proteins. The tendon layer certainly had to be capable of withstanding large strains, because the bows were up to 3 cm thick, giving the tendon layer a high second moment of area, and these bows were bent into a curve with a relatively small radius, when fired, imposing large strains on the tendon layer.

Today, the only collagen composites being manufactured are those for the medical industry where collagen, has been used to make prosthetic ligaments, that can act as a scaffold for the re-growth of new tissue [6], and to make artificial skin [8]. However, these materials are highly hydrated and therefore have very different properties from the composite described earlier.

In this paper, we will describe the manufacture of tendon/animal glue composites and investigate their tensile behaviour to determine whether this material is really capable of storing large amounts of strain energy and is as damage tolerant as reputed. Mechanisms of damage tolerance will be considered.

2. Methods

Tendons were obtained from freshly killed cattle. Only the lower leg tendons were used. Each tendon was cleaned of muscle and fat before being left to air dry at room temperature for 4 weeks. The dried tendons were then beaten with a wooden mallet to initiate separation of fibre bundles. Bundles were picked out by hand and stripped into finer fibres by carefully tearing them apart longitudinally. Bunches of fibres were hand combed into a parallel alignment and then cut into 5 cm long sections (this gave each fibre an average aspect ratio of 200, see Section 3 for fibre diameters). The final fibrous material was characterised by selecting a small sample of fibres and embedding them, unidirectionally, in epoxy resin. When dry one end of the block was polished on a sanding disk until the cross sections of the fibres were exposed, allowing the cross sectional areas of the fibres to be examined with a light microscope. The diameters of all the fibres in the section were measured.

Pearl glue, a commercial animal glue, manufactured by boiling animal hides, was combined with the tendon fibres to form composites. Granules of dry glue were soaked in an equal volume of water for 12 h to form a stiff gel. This gel was melted by gently heating over a gas flame and the hot molten glue was combined with tendon fibres. Two different treatments were tried at this stage for comparison; half of the bunches of prepared tendon fibres were moistened under a tap while the other half were kept dry. Dry or wet bunches were kept separate and placed into the bottom of rectangular moulds. Bunches were laid next to one another in an overlapping manner and once a single layer of tendon fibres had been formed hot glue was poured over them. If necessary a second layer of tendon and glue was built up over the first. The composite was then left to set. At room temperature the glue forms a gel within 1–2 min. However, this gel time could be extended by heating the mould to 40 °C (excessive heating can damage the tendon). The composite was allowed to dry for 4 days before testing.

A second batch of fibre was prepared as described above, however, the volume fraction of tendon and glue was varied by adding different known weights of dry tendon and then pouring on a pre-determined weight of glue. Dry composite specimens were also weighed allowing the volume fraction of tendon to be double checked.

Specimens were formed as long narrow strips (15 cm long and 7 mm wide). To ensure that the specimens were not damaged when they were clamped into the test machine, four aluminium stubs were glued to the ends of each strip of composite, using Araldite as shown in Fig. 1. The specimens were tested in a tensile mode using an Instron 4202 testing machine. Stress was calculated from the load and initial cross-sectional area, while strain was calculated from the length of specimen between the grips and cross-head displacement. Stress and strain were continuously plotted as the specimens were stretched to failure at a rate of 10 mm/min. The damage sustained by specimens after different amounts of applied strain was examined using light and electron microscopy.

Some composite specimens and whole dry tendons were cyclically tested by loading them to specified strains and then unloading them at the same rate. Recovery time of 30 min was allowed, before a second loading cycle was carried out. The procedure was repeated until large strains of up to 20% were reached (Fig. 10).

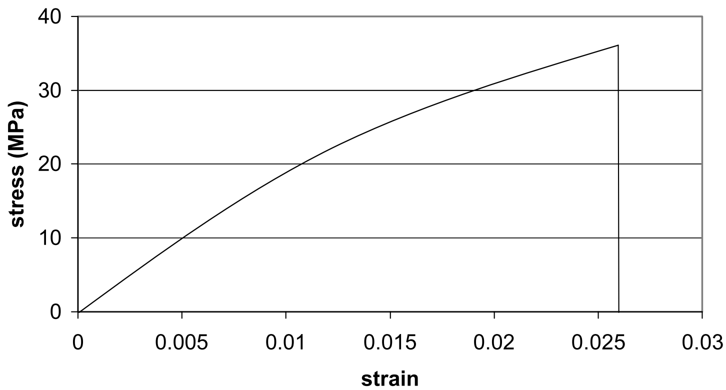

Fig. 2. A typical stress/strain curve for dry pearl glue tested in tension.

Dry whole tendons and samples of dry pearl glue were also subjected to tensile tests as described earlier.

3. Results

Dry pearl glue was found to have a mean tensile modulus of 2.11 GPa (SD = 0.26, $n = 6$) and mean strength of 31.8 MPa (SD = 6.3, $n = 6$). The mean failure strain was 2.9% (SD = 0.7, $n = 6$). Throughout this paper, strength is defined as the peak stress and tensile stiffness was calculated as the slope of the steepest portion of the stress/strain curve (which for all the materials examined here occurred at between 0 and 2% strain). A typical stress/strain curve for dry pearl glue is shown in Fig. 2. Dry tendon was found to have a mean tensile modulus of 2.41 GPa (SD = 0.31, $n = 5$) and mean strength of 180 MPa (SD = 24, $n = 5$). The mean failure strain was 25.6% (SD = 2.7, $n = 5$). A typical stress/strain curve for dry bovine tendon is shown in Fig. 3. The curve shows the s-shape characteristic of many biological materials, often explained by the re-orientations of components within the material.

The average diameter of collagen fibres used in the manufacturing of composites was found to be 254 μm (SD = 73, $n = 55$). This average dimension corresponds to a fibre composed of smaller fibrils of dimensions 5–20 μm. These fibrils were observed to be loosely held together to make up the larger fibre with many gaps between fibrils, into which matrix material could easily penetrate. The fibres were all of equal length (5 cm) due to the mode of separation from the tendon.

Tendon/glue composites formed with wet fibres at a fibre volume fraction of 50% were found to have a mean tensile modulus of 2.32 GPa (SD = 0.44, $n = 12$) and mean strength of 100 MPa (SD = 17.3, $n = 12$). The mean failure strain was 20.6% (SD = 6.2, $n = 12$). Tendon/glue composites formed with dry fibres at 50% volume fraction had a significantly lower modulus and strength than those formed from wet fibre and failed at much lower strains. The mean tensile modulus was found to be 1.02 GPa (SD = 0.7, $n = 8$). The mean strength was found to be 47.5 MPa (SD = 2.9, $n = 8$) and the mean failure strain was 4.8% (SD = 1.7, $n = 8$). These specimens were visibly less well made, with areas where the glue had not properly penetrated between the fibres.

The force deflection curve for a typical composite specimen formed with wet fibre at a volume fraction of 0.5 is shown in Fig. 4. The curve can be divided into two parts. The first part, up to a strain of 2% has a slightly increasing slope. Beyond this the slope declines and fracturing of the matrix begins, resulting in small drops in the load, followed by recovery. It is interesting to note that the initiation of failures does not cause the underlying trend of the curve to develop a negative slope. Instead the trend continues to be positive but with a much reduced slope compared to part one.

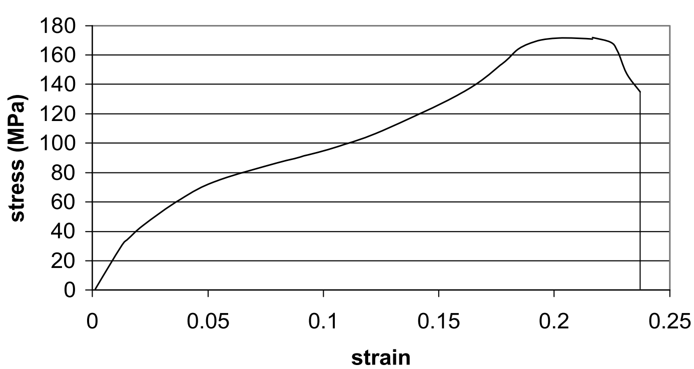

Fig. 3. A typical stress/strain curve for dry whole tendon tested in tension.

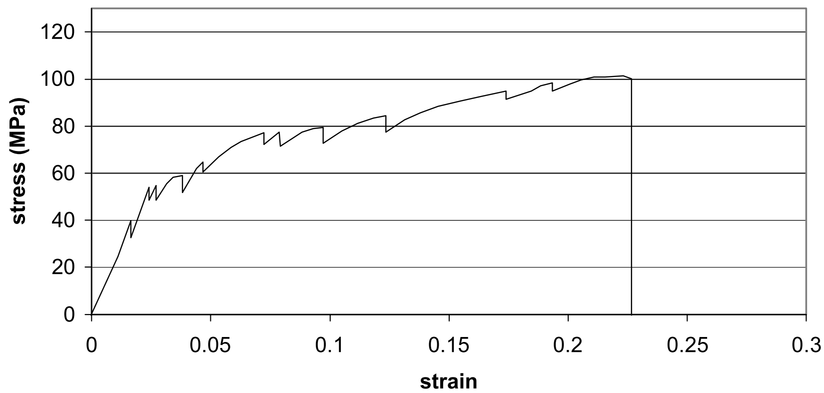

Fig. 4. A typical stress/strain curve for dry composite at a volume fraction of 50%, tested in tension.

After mechanical testing specimens were examined under a light microscope. The fracture surfaces of broken composite specimens showed a glassy fracture with little fibre pull out. In composite specimens that had been deformed to strains of greater than 2%, but not broken, many small cracks were observed within the matrix, running at right angles to the fibres. However, at composite strains of less than 6% the cracks were stopped when they encountered fibre bundles. Fig. 5 is an electron micrograph of a crack formed at high composite strains (18%) showing that fibres continue to bridge cracks as they open up and that fibres develop a kinked pattern after removal of the load (previously they were straight). The fibres do not fail or pull out of the matrix until the point of composite failure. However, some debonding of fibres from the matrix was observed on either side of large cracks, up to a distance of 5 mm, at high strains.

Fig. 6 shows a plot of composite tensile modulus as a function of tendon volume fraction. Not surprisingly there is no effect of tendon volume fraction on composite modulus ($R^2 = 0.036$) because the tendon and matrix have similar stiffness. However, if composite strength is plotted as a function of tendon volume fraction (Fig. 7) then it can be seen that the strength increases with increasing volume fraction ($R^2 = 0.613$). Failure strain and collagen volume fraction were found to be less strongly linked ($R^2 = 0.4$) over the range of volume fractions investigated (27–50%, see Fig. 8).

Fig. 9 shows the energy absorbed to failure by tendon/glue composites as a function of tendon volume fraction. Increasing the volume fraction of tendon increased the energy absorbed ($R^2 = 0.706$) mostly because strength had increased, but also due to an increase in failure strain. The maximum energy absorption recorded was 18 MJ/m^3.

Repeated loading and unloading of whole dry tendons to different levels of strain between 1 and 20% (Fig. 10) showed that up to 5% strain the specimens behaved elastically and there was no irreversible deformation or reduction in energy absorbing capability. However, at 10% strain the specimens were found to absorb 5% (SD = 2%, $n = 5$) less

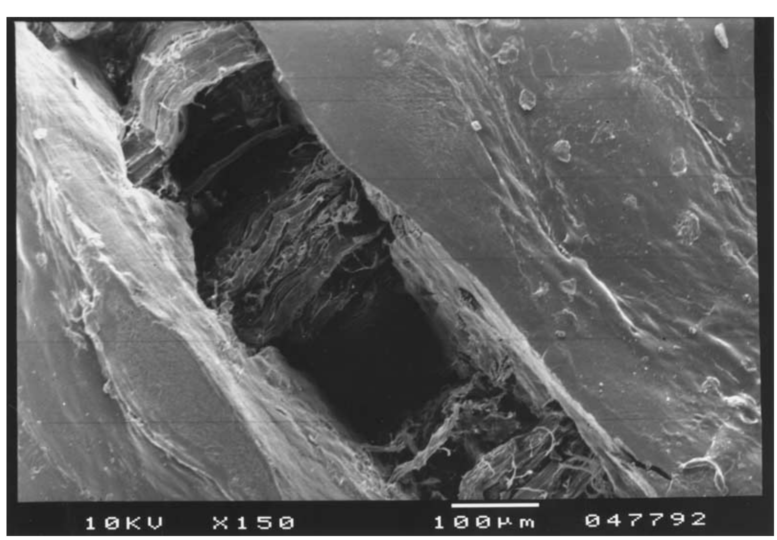

Fig. 5. An electron micrograph showing a crack in tendon/glue composite deformed to a strain of 18%. Collagen fibres can be seen bridging the crack and the crack has not closed up after removal of the load, indicating that irreversible deformation has occurred.

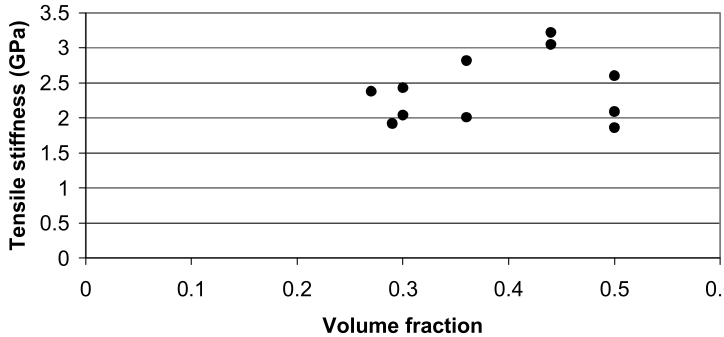

Fig. 6. The stiffness of tendon/glue composites plotted against tendon fibre volume fraction.

energy during a second loading. Tendon glue composites with high volume fractions of fibre (50%) behaved in a very similar way, during loading and unloading experiments. The composites behaved elastically up to 1.5% strain. At strains greater than 1.5% there was increasing irreversible deformation, however, this remained very small (less than 1% of initial failure strain) until specimens had been deformed to 10% strain. The change in energy storage capacity on subsequent loading was more obvious, for example at 6% strain there was on average a 3% ($SD = 2\%$, $n = 5$) reduction in energy storing capacity. For loading cycles of $n > 4$ there was no measurable change in energy absorption at 6% strain.

4. Discussion

The properties of tendon/glue composites were much improved by using wet tendon fibres during the manufacturing process. This greatly increased the stiffness, strength, failure strain and the energy absorbing capacity of the composites. The reason for this is probably that the molten glue is able to diffuse into the wet fibre bundles forming a much stronger interface and leaving fewer resin deficient regions.

Tendon/glue composites made with a 50% volume fraction of collagen fibres showed a maximum energy absorption of 18 MJ/m^3. This compares well with CRP and GRP that absorb around 20–30 MJ/m^3 and is higher than thermoplastics and thermosetts that absorb energy in the range 1–10 MJ/m^3. The stiffness of the composite is low compared to GRP, being similar to synthetic thermoplastics and thermosetting materials (2.5 GPa). However, the composite can achieve much higher strains than GRP, CRP or many thermoplastics and given its low modulus it has a very high strength. The composites large failure strain is controlled by the tendon fibre content. Dry intact tendon can achieve very high failure strains of greater than 25% while dry pearl glue has a failure strain of only 2.9%, similar to synthetic thermoplastics. The tendon is also more than five times stronger than the glue. Therefore as the volume fraction of tendon fibre is increased, the strength of the composite increases and the energy absorbed to failure rises.

The stiffness of animal glue and tendon in the dry state is similar. At first sight this seems strange because the molecular order in tendon is much higher than in the disordered (denatured) glue. However, in tendon the molecules are organised into a zig-zag conformation that progressively opens out with increasing strain, thereby reducing the modulus. This also explains the large strain elasticity of the tendon. It is also possible that there may be some slippage between fibrils, at very large strains, within the hierarchical organisation of tendon, introducing a plastic component to the deformation. However, this requires further investigation.

The composite described in this paper is very different

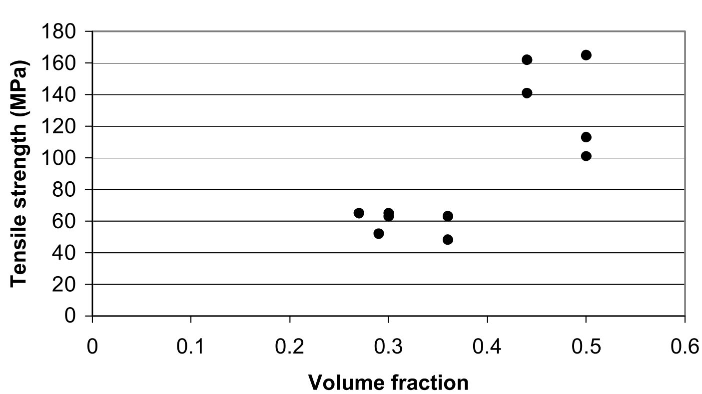

Fig. 7. The strength of tendon/glue composites plotted against tendon fibre volume fraction.

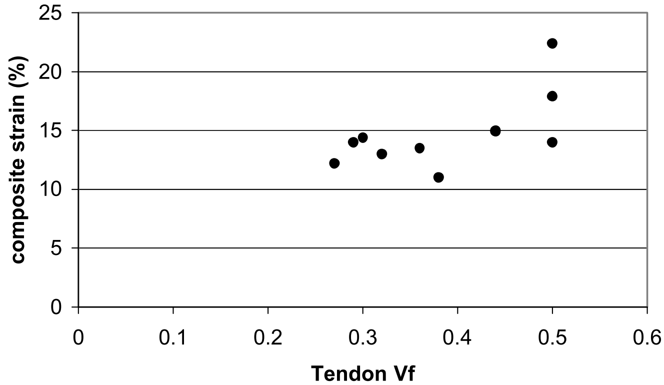

Fig. 8. The failure strain of tendon/glue composites plotted against tendon fibre volume fraction.

from traditional engineering composites because the fibres do not increase the stiffness of the composite, instead increasing strength, failure strain and energy absorption. The mechanism by which they do this may be similar in some respects to the mechanism used to toughen ceramics by adding ductile metal fibres [9]. It is clear from our evidence here that the collagen fibres act as crack stoppers at low strains and continue to bridge cracks at higher strains. There is some debonding of the fibres, but only within a zone extending a few millimetres either side of the crack. At very large composite strains, e.g. 18% as shown in Fig. 5, there is evidence that the fibres have stretched plastically across the opening crack. This can be seen when the composite is unloaded because the cracks partially close but the fibres remain stretched and are thus forced into a kinked shape. Therefore we postulate that the matrix fibre interface is strong and that when a propagating crack reaches a fibre the crack is stopped and deflected along the fibre so that some debonding occurs between the fibre and matrix. The energy required to do this will be unrecoverable and could account for the small amount of energy lost if the specimen is unloaded and then re-loaded to the same strain. However, debonding is probably limited by the high strength of the interface and once a short length of fibre has been released from the matrix, that section of fibre is able to stretch elastically (and at large strains plastically), with a relatively low modulus, allowing the crack to progress further but in a controlled manner that requires more energy than before. This enables the composite to continue to be dominated by elastic behaviour even after previous large deformations and significant microcracking. The crack stopping mechanisms do not operate in the same way if the fibres are not wetted during the manufacturing process. Wetting the fibres probably allows the glue to form a much stronger association with the fibres. If the bond between the fibres and matrix is too weak then cracks will propagate along the interface between fibres and matrix and the fibres will pull out at low composite strains, rather than being forced to stretch across the opening cracks. This theory is supported by the fact that a more fibrous fracture surface was observed in the composites formed from dry fibre, indicating that there was more fibre pull out.

The kind of crack bridging described earlier has been achieved in synthetic composites by using metal or polymer fibres that can deform plastically across an opening crack and there are good theoretical models for how this works [10,11]. However, in the system being investigated here there is less plastic deformation of fibres, instead the tendon fibres are able to stretch elastically to large strains of 10% or more. Repeated loading and unloading tests on whole dry

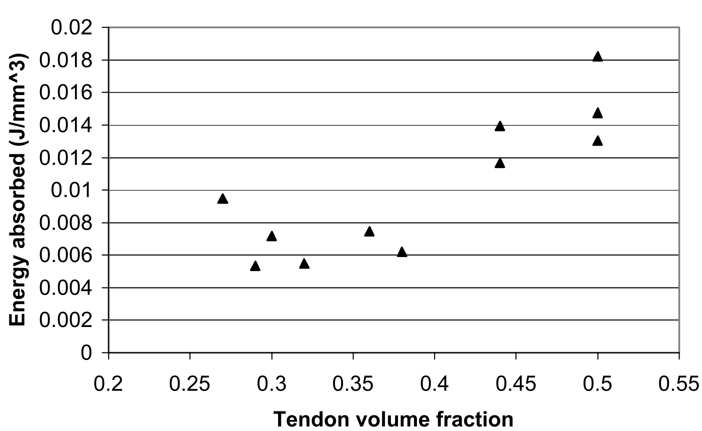

Fig. 9. The energy absorbed to failure by tendon/glue composites plotted against tendon fibre volume fraction.

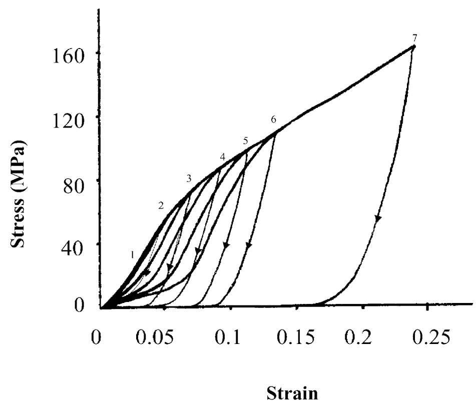

Fig. 10. Stress strain curve for a whole dry tendon repeatedly loaded and unloaded in tension. The numbers show the magnitude to which successive loads were applied and the direction of unloading is indicated by arrows.

tendons (Fig. 10) showed that 95% of the energy absorbed by the tendon during large deformations of 10% was stored as elastic strain energy, with the remaining 5% being absorbed irreversibly, probably as plastic work and work of fracture. Therefore, tendon composites with a high volume fraction of tendon fibres are also dominated by elastic energy storage, even at large deformations which result in the formation of small localised cracks in the composite but little fibre–matrix debonding. This explains why this natural composite is ideal for backing archery bows, allowing the energy put into bending the bow to be stored in the tendon layer and transferred to the arrow upon release of the string.

More work is required on tendon/gelatine composites to measure the strength of the fibre–matrix interface and to measure the work of fracture using standard fracture tests.

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