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Woolrock—a material for technical use consisting of keratin

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Abstract This article debates the production of mouldings made of keratin. It is demonstrated that the properties of keratin allow for being processed with heat and pressure to manufacture tough mouldings without chemical preprocessing of the used wool. This material thus has a high potential as a bioplastic, because it potentially can be used with conventional plastic manufacturing techniques. Additionally, it might also serve as an adhesive in various applications. The biobased material might become a sustainable source for mouldings.

Introduction

The utilisation of biobased materials has a long tradition and mankind has always used renewable resources. Often these materials have been easily accessable, like for instance wood, and did not require much processing. A precursor of modern efforts in the development of high performance biobased materials can be seen in the early 20th century chemurgy [1] which investigated new applications for agricultural products.

As introduced by Anex [2] in a special issue of the 'Journal of Industrial Ecology' biobased products may help to reduce the dependence on nonrenewable materials. Thus they are an important factor towards sustainable development. Much effort is put in this field today and whole institutions turn their focus on renewable resources, like our Center for Appropriate Technology. This can be called a renaissance of biobased materials. For a broad overview on biodegradable plastics see for instance Stevens [3].

A variety of materials is already on the market, like polylactic acid (PLA), polyhydroxy butyrate (PHB), natural resins, starch and lignin based materials, just to name a few. They are all biobased, renewable and biodegradable if not blended unfavourably. Many of them show thermoplastic behaviour and can thus be used with conventional plastics processing machines. The products made of renewable resources have a broad spectrum of properties with differences in terms of energy effort for production, strength, density, duration of biodegradation or water resistance, and can be used in various fields of application.

Our work focuses on proteins like keratin and their potential as biobased materials which also possess some properties that are comparable to conventional plastics. Keratin, as found in wool, requires a rather low amount of energy to be produced by the sheep [4, 5], which is a good starting point for products developed within the scope of sustainable development. Also the performance of the raw material wool concerning other parameters, like thermal conductivity, is extraordinary.

Furthermore the availability of even larger amounts of wool for biopolymer use is guaranteed due to the fact that currently (in the industrialised European countries) untreated sheep wool is seen as a low value side product and often dumped. This shows that there is quite a potential in economical terms in this material which today is not even used as a byproduct.

The topic of our work was to find out the behaviour of wool under heat and pressure and to investigate whether the material could be used as a thermoplastic biopolymer.

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Keratin as the basic material

Keratin is the name for a group of fibrous structural proteins consisting of a variety of amino acids with a relatively high amount of disulfide bonds formed by cystine, which is responsible for its high stability. The peptide chains are interlinked with each other and so the whole material is stabilised. Keratin is found especially in vertebrates and is a main component in horn, hair, fingernails, hooves, feathers and skin. According to Vincent [6, p.44] keratins can be divided into the three groups of mammal, bird and other keratins like those found in reptiles. Research on sheep [7] has shown that chemically horn and hooves are very similar, while wool consists of the same amino acids but with slightly different ratios of occurrence. Wool contains more sulphur (i.e., cystine) than horn or hoof.

Manufacturing products out of horn has a long tradition (frames for eyeglasses, knobs, etc.). By use of heat the material is softened and can then be shaped by bending or pressing it into a desired form [8, 'Horn'].

At normal atmospheric pressure keratin does not have a clearly defined melting point and pyrolysis starts from 150 to 200 ° C[1].

In the experiment described below we investigated the effect of heat and pressure on keratin, focusing on melting the material.

Similar approaches

A first patent search brought one result [9] which looked similar to our approach, but a closer look at the Hungarian patent made clear that modifications by additional chemicals are applied to the keratin material.

After that a patent investigation at the Austrian Patent Office was ordered, questing for 'pressed formed parts (injection moulding, extrusion, hot pressing) of keratin (wool, horn, feathers, hair) or chitin, where the material is changed to a plastic deformable condition by pressure and heat'. None of these patents are in conflict with our approach—manufacturing of wool without chemical treatment.

The result, a list of ten patents, is shortly mentioned in the following: In patent [10] a soluble keratin fraction is produced by breaking the disulfide linkages and by later removing the solvent and oxidising sheet cross-linked keratin. The patent [11] looks similar to our approach for it uses elevated temperature and pressure but a medium is needed. Patent [12] is not relevant to our case because it deals with chitin. In patent [13] a process is described which needs additional chemicals. Patent [14] calls for an oxidant. Patent [15] also calls for additional chemicals like resin-like compositions. In patent [16] preprocessing of keratin is covered by means of crushing, grinding and milling, but for making moulded articles, keratin is generally mixed with artificial resins. Also in patent [17] chemical alterations are performed, in this case with a diisocyanate or aldehyde compound and polyethylene oxide. In the patent [18] 1–40 wt.% of a natural organic substance is used, which means that a mixture of different materials comes into place. In patent [19] a maximum of 95 wt.% of fibrous keratin and additionally up to 50 wt.% arbitrary additives are processed.

A literature search resulted in a paper by Katoh et al. [20] who work on films where keratin is a basic material, but here also additional chemicals are added in the process.

Furthermore there is a company in New Zealand named Keratec[2] which might use a related approach, but since this is a proprietary process we can not tell whether there are similarities or not.

Pressure and temperature tests

For the experiments wool fleece was used. This raw material was acquired from a mattress manufacturer who uses only soap washed but not chemically or otherwise modified wool.

The wool fleece was filled into a piece of steel tube with an inner diameter of 30 mm and a length of 200 mm. With a short steel piston at the bottom and a longer at the top the inside room was closed. The play between piston and tube was 0.1 mm. This arrangement was put into a press for applying force in axial direction to compress the wool. Figure 1 shows how the experiment was performed. At the outside of the tube with a wall thickness of 5 mm two temperature sensors (thermo couple) where mounted, the first 20 mm and the second 100 mm away from the bottom of the tube, to allow control of a homogeneous temperature distribution.

While the pressure on the wool was kept in a range of 35–55 MPa heat was applied to the top of the tube. The tube was heated up at the top sensor by a rate of about 10 K/min while watching the movement especially of the top piston. With the two temperature sensors the temperature inside and thus the temperature of the wool was ascertained. The sensors also allowed for keeping the difference in temperature between top and bottom side as low as possible for more precise estimation of the inside temperature.

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[1] http://www.textile-warenkunde.de/Flammschutz%20auf%20Textilien.htm

[2] http://www.keratec.co.nz

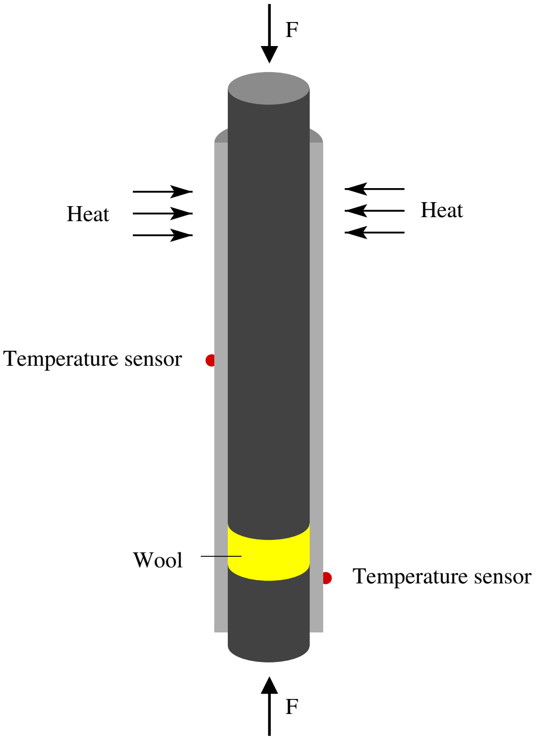

Fig. 1 The arrangement of the experiment. The steel tube was filled with wool, from top and bottom two steel pistons were inserted into the tube and the whole apparatus was put into a press to apply axial force. Two temperature sensors were mounted to the outside of the tube and heat was applied only at the top. The picture shows the situation at the end of the experiment where the wool was already compressed

Results

After about 20 min of heat supply, when the temperature at the top sensor reached 220 °C, the top piston jerkily moved into the tube indicating a distinct compression of the wool. The temperature at the bottom sensor at that time was 140 °C.

During the compression phase material flowed through the slit between piston and tube up to the top and leaked out at the top end of the tube. At this moment also vapour started to emerge out of the tube. The distance to cover for the material in the 0.1 mm slit was about 120 mm. Although some material leaked at the bottom as well, more came out of the top. This is probably due to the higher temperatures in the top area.

After cooling down the specimen was taken out of the tube. The tube showed deformation in radial direction in the area that surrounded the wool, i.e., it bulged. This plastic expansion of the steel tube indicates that increasing pressure in radial direction occurred which possibly was the result of melted wool.

The wool fleece itself had turned into a 10 mm thick solid disk. The brownish material looked very much like horn, where the wool fibres were no longer visible with bare eye.

One specimen was put into water for some days. After a few hours it became softer but kept its shape and did not dissolve in water. When it was dried again it hardened and showed the same properties as before.

It was also found that the material stuck very well to the steel surface and by flowing into the slit it glued together tube and pistons after it was cooled down.

The experiment shows that in a temperature range which is very close to that of pyrolysis and a pressure of 35–55 MPa keratin becomes plastified or even liquid. The wool changed from loose fibres to a stiff and hard product with the shape given by the mould.

Immediately after releasing the material from the moulding it was smelling quite intensively, but after some days no odour was left. During the tests the material might have experienced temperatures higher than necessary for moulding. So probably the generation of smell can be reduced with lower processing temperatures.

Macroscopic properties

The specimens of the experiment look very much like big horn knobs. They are tough, hard and stiff, with a dull brownish surface, and also homogeneous, which was found when cutting through a specimen. The density of the pieces is slightly higher than 1.1 g/cm^3. The inner structure macroscopically is not different from the appearance at the surface. The shape is exactly that of the given mould and the specimens are stable in shape. It is possible to cut or drill the specimens with ordinary wood processing machines. The properties can be listed as follows:

- tough
- stiff
- relatively hard
- homogeneous
- stable in shape
- mouldable
- cutting, drilling, etc. possible
- water resistant

In Fig. 2 the surface of a specimen which was released from the tube when it still was hot is shown. In this case where the material hardend in air without applying further pressure gas bubbles inside the material expanded and thus the surface became smooth and shiny. The material of this specimen became porous with low density but still it is tough. This is another indicator for liquefied parts in the wool.

Microscopic observation

Some material of a specimen which was demoulded after cooling down to ambient conditions was cut off the surface

Fig. 2 Melted surface of a specimen which was released hot from the experimental arrangement, so there were liquid parts which hardened in air under ambient conditions. Inside the material is porous but still tough. The area shown is about 20 mm wide

and observed under the microscope. In Fig. 3 a microscopic image is depicted. This clearly shows that some wool fibres did not melt. But also gas bubbles in a matrix are seen which indicates that the wool partly became liquid during the procedure of applying heat and pressure.

Wool as bioplastic

According to this results it might be possible to utilise pure wool as a biobased material in producing plastics mouldings.

The material can probably be pressed into any given mould. Its plastic-like behaviour could thus be used in injection moulding or extrusion. As the experiment shows the material can flow over 120 mm through a tiny slit of 0.1 mm, therefore the flow ratio is at least 1200:1 (considering that the play was not getting bigger which is plausible because the warming up took long enough for heating up the pistons to the same temperature as the tube) which is relatively high compared to some other bioplastic materials with e.g., a wooden component.

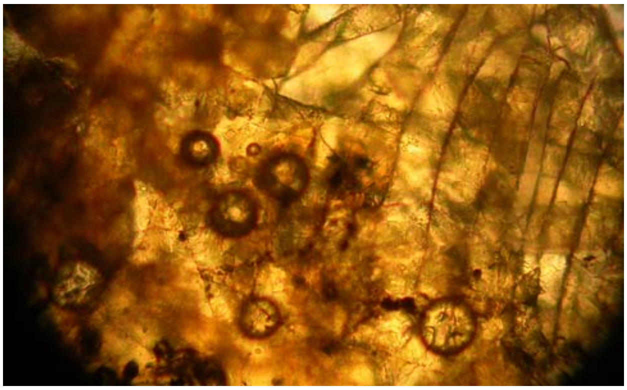

Fig. 3 The microscopic image of a specimen which was cut off from the surface of a hardened specimen shows that some wool fibres did not melt. But also gas bubbles in a matrix are seen which indicates that the wool became liquid during the experiment

As we have seen in the experiment where the specimen was released in hot condition gas bubbles expanded on the surface (see Fig. 2). This indicates that even the production of foams seems to be possible. So applications could cover a range of requirements from solid homogeneous products to lightweight porous ones.

The material most probably remains biodegradable. This has to be tested in further research, but taking into account the source and the processing with solely applying pressure and temperature the chemistry may not change much. As the surface is reduced when changing from fibrous structure to a solid piece the period of time for degradation is supposed to be longer than that of the original wool. Materials of keratin are not rapidly degrading when compared to other renewable resources [21,p.296]. This property allows for long living products without any special treatment like coating.

By blending wool with other biomaterials certain characteristics, from duration of biodegradation, over density and thermal conductivity to mechanical properties, can possibly be adjusted to the required properties of specific products.

Wool as adhesive

Due to the interesting property of the melted wool adhering to steel the wool might also serve as a glue, very similar to state-of-the-art hot-melt adhesives. Keratin may then serve not only for gluing together metal parts but also other materials, and there is a broad field of applications in areas where no synthetic or toxic products are desired. The adhesiveness may also lead to composite materials that are fully made of renewable materials. The liquefied wool can be thought of as a matrix for fibre-reinforced plastics for instance in combination with the very tough hemp fibre.

Outlook

Many of the known biobased materials that are used in technology have the great disadvantage that they are not water resistant. This, as is our experience, is often the reason why the bioplastics already on the market are not suitable for many applications. The material described in this article is water proof. If intensively exposed to water it softens but the shape remains and when dried again it regains its original properties.

Furthermore the production of other biobased materials that are already on the market is rather complicated and thus they are costly; one just has to think of PLA which must be manufactured biotechnologically in a fermenter. Compared to that the manufacturing technique described above is quite simple and does not require much preprocessing. As the raw material today is wasted it might also serve as a cheap alternative to other materials.

Although other keratin biomaterials contain less disulfide bonds it is quite reasonable that also feathers, horn or hooves can be used in the same way as wool. Even hair might be a resource. This would broaden the range of raw materials for a new bioplastic.

The compressed solid wool, referred to as ‘woolrock’, might have some potential in leading towards a more environmentally friendly production towards the goals of sustainable development. The resource is renewable, the effort for production is relatively low and untreated material might be recycled or released to the biosphere, i.e., composted.

For achieving this further research has to be done firstly to find out the exact conditions under which ordinary wool can be processed especially concerning temperature and pressure range. These characteristics can be found out with simple, straightforward test series. The degree of liquefaction can thereby be observed with optical microscopy.

As the material is potentially usable with conventional plastic manufacturing machines, secondly, the proper techniques have to be found. Besides injection moulding and extrusion the process of hot-pressing looks very promissing. But also foaming techniques should be investigated. This must be followed by investigating the specific requirements and adjustments for the processes that fit best. The requirements have to be examined and quantified by test series where emphasis must be laid on the adhesiveness of the hot wool. A proper way has to be found that allows using a mould several times, either by means of temperature regulation, coating and/or appropriate release agents.

Third, the properties of the products need to be observed. Especially the mechanical properties have to be investigated with respect to different processing parameters. Thus it can be found out at which temperature and pressure the wool starts to degrade and certain mechanical features start declining. These data can by iteration be used to refine the processing adjustments. But also other relevant features like thermal and electrical conductivity as well as biodegradability have to be investigated.

Fourth, the adhesive properties have to be investigated. Again based on the examined temperature and pressure range simple tests can be made with state-of-the-art equipment. Thereby, on the one hand, the processing conditions have to be investigated together with the eventual use of additional agents. On the other hand it has to be investigated which materials can be glued together and how strong the adhesive forces are.

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