Investigation of eco-friendly casein fibre production methods

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Abstract: The growing environmentally awareness of the consumers leads to a lot of new products in the textile industry. Either a sustainably produced textile or one which is created by reuse of a waste product is preferred. One possibility to create fibers from waste is using waste milk for casein fiber production. Opposite to several other biopolymers, however, spinning fibers from casein causes diverse problems. This article gives an overview of the investigations on how to produce fibres from the milk protein casein in a sustainable way, i.e. without formaldehyde or other polluting ingredients. Mechanical properties as well as water-resistance were investigated for chemical and physical modifications of the base composition. In this way, the positive influence of paraffin oil and wax as well as aggregation at high temperatures could be proven, while temperature treatment resulted in a higher E-modulus.

1. Introduction
Approximately 2 million tons of milk are thrown away every year only in Germany. This waste milk still contains 2.8-3.2 % of the protein casein which was already used for fibre production in the 1930s. But at that time casein fibres were produced with formaldehyde, the process needed a lot of water and the production could not be made profitable; a problem which is not yet solved [1]. Over the last years new methods were found to produce these fibres in a more eco-friendly way and a newly developed process without using formaldehyde is described in a recent patent [2]; however, these fibres are co-spun together with viscose or wool. In electrospinning, casein can be used in combination with other materials [3,4] or in graft copolymers [5], again with weak water resistance. On the other hand, casein is able to absorb water which gives a smooth sensation on the skin and makes it comfortable to wear. Especially people with skin diseases such as neurodermatitis would benefit from this clothing. It is also reported that casein has a natural antibacterial effect. Additionally, casein can be used to attract macromolecules (i.e. proteins, polysaccharides, etc.) and to work as a size-selective molecular device [6]. In the form of a multilayer film, it has been reported to promote biomineralization [7]. This opens a wide range of new possibilities in the medical sector. Due to these properties of textiles containing casein, more investigations should be performed to increase strength and water resistance of casein fibers. However, crosslinking with citric acid should be avoided since these fibers are known to be cytotoxic [9].
In previous investigations casein powder was mixed with water in different proportions, stirred, slowly heated up to 75 °C and spun by hand extrusion through nozzles of different diameters as well as used as coatings on different textile fabrics [8]. To reduce brittleness of the resulting fibre, different amounts of glycerine were added to the solution.
This resulted in significantly different viscosities depending on the casein-water proportion. In all cases, the necessity to add the casein to heated water in small amounts during stirring emerged. Independent of the mixing ratio, the resulting fibres or textile coatings were quite hard and brittle. The coated textile fabrics showed a water resistance of up to 33 minutes.

To improve the results, another chemical approach was tested in this paper.

2. Materials and Methods
Technical casein from bovine milk containing 90 % protein (Sigma, St. Louis, USA) was ground in a mortar and filtered through a sieve with 200 µm mesh size. Viscous paraffin oil from Roth (Karlsruhe, Germany) and glycerol (99.8 %) from alexmo cosmetics (Weyhe, Germany) were added in most recipes. Partly, glucose or wax (KahlWax 6592, Trittau, Germany) were added. For all compositions, glycerol was mixed with equal amounts of distilled water. Casein was added under stirring at 500 rpm at room temperature. Depending on the recipe, other ingredients were added. The pH value of this mixture was carefully adjusted to pH 6.5, using 0.5 M NaOH since casein is soluble in water only above pH 6.4. After the casein was completely dissolved, the mixture was heated to 65 °C to decrease viscosity and allow formation of fibers through a spinning nozzle.

Table 1 gives an overview of the different recipes under investigation in this study.

| Sample | Glycerol 50 % | Casein | Paraffin oil | Glucose | Wax |
|--------|---------------|--------|--------------|---------|-----|
| 1      | 20 ml         | 10 g   |              |         |     |
| 2      | 20 ml         | 10 g   | 5 ml         |         |     |
| 3      | 20 ml         | 10 g   | 2.5 ml       |         |     |
| 4      | 20 ml         | 10 g   | 1 ml         |         |     |
| 5      | 20 ml         | 10 g   | 5 ml         | 10 g    |     |
| 6      | 15 ml         | 10 g   | 5 ml         |         |     |
| 7      | 20 ml         | 10 g   |              |         | 5 g |
| 8      | 20 ml         | 10 g   | 5 ml         |         | 5 g |

The produced fibers had diameters of approx. 1 mm, according to the relatively large spinning nozzle which was chosen due to the high viscosity of the spinning solution. Additionally, in this way significant influences of small deviations of the fiber diameter on the tests of mechanical properties and water solubility could be avoided.

All samples were dried in two different ways: placement on a PTFE foil at room temperature, and drying on a PTFE foil during temperature treatment using a heat gun.

Mechanical tests were performed using a Sauter universal test instrument, mounting the casein fibers with a free clamping length of 50 mm and elongating them at a speed of 5 mm/min.

Water resistance tests were carried out by inserting the fibers into water for different times between 0 min and 60 min. The fibers were then dried in an oven for 36 h at a temperature of 65 °C. Comparing their masses before and after the test allowed calculation of their absolute and relative losses of mass, respectively. The tests were performed 3 times per fiber.

3. Results and Discussion

Figure 1 depicts exemplary results of investigations of the mechanical properties of casein fibers, produced according to Table 1 and dried at room temperature or during heating, respectively. Generally, there is a tendency towards higher elongation for the fibers dried at room temperature, while the highest breaking forces are reached for the hot dried fibers no. 2 and no. 7, prepared with the highest amount of paraffin oil and wax, respectively.

Compared with other casein fiber investigations, the tensile strength of the fibers produced here is approx. one order of magnitude lower. This may be attributed to small air bubbles which are visible in
all fiber cross-sections. Apparently, in a next step, the amount of air in the spinning solution must be reduced, e.g. by using ultrasonic degassing after heating or by stirring in vacuum.

![Figure 1](image1.png)

**Figure 1.** Stress-strain curves, measured for casein fibers produced from different recipes (table 1) and dried at different temperatures.

In the tests depicted here, the main focus was not on high breaking forces, which are not necessary for diverse applications in the medical sector. More important is the possibility to tailor the water solubility, especially for drug release or similar medical applications.

Figure 2 depicts the results of the respective tests. Here, especially the results of the longest immersion time show differences between the different chemical compositions of the samples and the temperature treatment during drying. Relatively low mass losses were reached for sample 2 as well as sample 7 after hot drying. Apparently, wax as well as paraffin oil support water resistance, while glucose – which was reported by another group to help crosslinking [10] – does not show any effect on the water resistance of the gained fibers.

![Figure 2](image2.png)

**Figure 2.** Relative mass loss, measured for the samples described above after drying at different temperatures, after immersing in water for different times.

Although the results depicted here are not yet sufficient for an application of casein in most medical applications, the experiments show that increasing water resistance of casein is also possible without adding citric acid.

4. Conclusion
To conclude, we have investigated the influence of different chemical ingredients and temperature treatment on casein fiber production. The mechanical properties are significantly lower than in other biopolymers which are in the order of a few cN/dtex, i.e. a few hundred MPa [11], but one order of
magnitude higher than foams from microcrystalline chitosan [12], suggesting their use in medical applications which do not necessitate high mechanical strength, e.g. in wound healing, drug delivery or for tissue engineering. Chemical modifications as well as temperature treatment resulted in significantly increased water resistance, showing a way to possible eco-friendly production methods of casein fibres without formaldehyde or cytotoxic citric acid.

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