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Manufacturing Possibilities of Silk Paper for Antique Fabric Conservation

Abstract
In this study, the conditions and results of silk fibre modification with the use of proteolytic enzymes are presented. Using the technique of scanning electron microscope (SEM), it was shown that the enzymatic treatment resulted in clear fibrillation of the silk fibre surface. The structural change in the surface of these fibres made it possible to process them by the paper-making method to obtain homogeneous pulp (65% silk and 35% linters) and thin sheets of silk paper with a basis weight of 25 g/m^2. It was concluded that the silk paper obtained corresponds to the needs of conservators.

Key words: *antique fabrics, enzymes, fibrillation, SEM images, silk fibres, silk paper, surface structure.*

Introduction

Museum collections possess many antique fabrics that require a conservator's attention. Recently, one of the more often used methods for fabric conservation, also suitable for the conservation of antique silk fabrics, consists in sizing the fabrics onto sheets of very thin special paper [1, 2]. Due to their thinness (below 25 g/m^2), this paper is often called "silk paper" (Seidenpapier in German). They are manufactured from plant fibres, such as those obtained from the bast of any kind of mulberry (*Broussonetia papyrifera Vent.*), and manila fibres obtained from banana leaves (*Musa textilis*) [3]. In spite of its name, "silk paper" contains no natural silk fibres [4]. The aqueous extract from "silk paper" is usually slightly alkaline (pH 6.8 – 8.0) [5]. The use of an alkaline material for silk fabric conservation may result in the hydrolytic destruction of fibroin – a protein substance of silk matter.

The Pulp & Paper Research Institute - ICP (presently a part of the Institute of Biopolymers and Chemical Fibres) in Łódź, in co-operation with the Academy of Fine Arts (ASP) in Warsaw attempted to make a paper-like material consisting of cellulose fibres and a considerable content of silk fibres. Such a possibility was confirmed, but it was difficult to prepare a homogeneous aqueous suspension of fibrillated cellulose fibres (linters) and silk fibres [6]. Hence, the silk paper obtained, containing about 65% silk, was characterised by considerable unevenness and an inadequate mechanical strength.

At the Department of Fibre Physics and Textile Metrology, studies were undertaken to prepare silk fibres for the paper-making process in a blend with plant fibres.

Experimental

The aim of the present study was to modify the surface structure of silk fibres and consequently to prepare a homogeneous pulp containing more than 60% silk, which is suitable for making thin sheets of *silk paper.* It was decided to use a biochemical method of silk modification using two proteolytic enzymes:

- Proteopol BP-S-100 (Pektovin, Poland),
- Alcalase 2.5L (Novozymes A/S, Denmark).

The enzymatic treatment of silk fabric samples was carried out using a laboratory dyeing machine Polymat (AHIBA). The conditions of modifications were as follows:

Enzyme:	(1.0 – 2.5) % on weight of fibres,
Na_2CO_3:	2.0 g/l,
Na_2HPO_4:	10 – 30 ml/l, (buffer: solution 1/15 M
Temperature:	45 ^{o}C,
Time:	10 – 90 min.,
Liquor ratio:	1 : 50,
pH of the bath:	8.2 – 8.5.

The final stage of the process was the inactivation of enzymes under the following conditions:

Temperature:	80 °C,
Time:	20 min.
pH:	~ 7.0.

The enzyme-treated samples were tested for:

- weight loss,
- tensile strength of silk fibres,

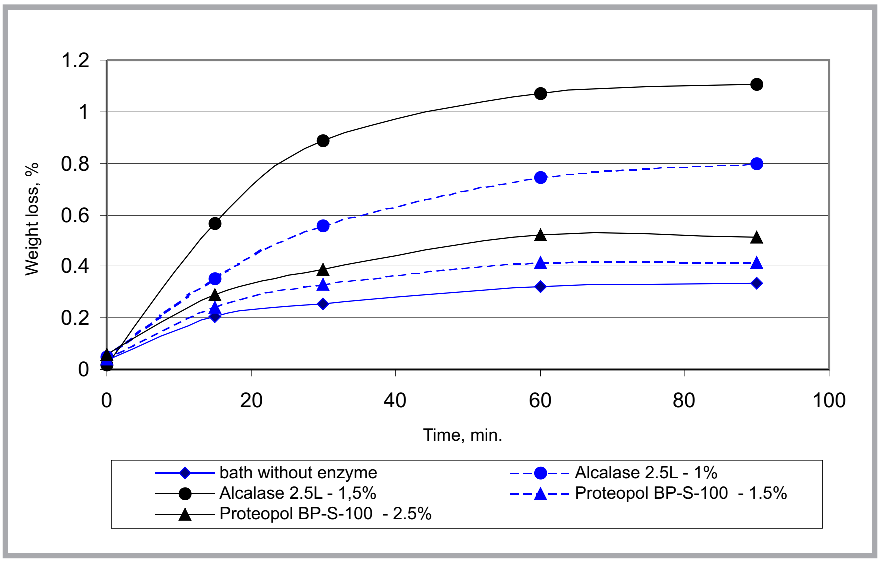

***Figure 1.** Weight loss of the silk fabric versus enzyme treatment time.*

Table 1. *Breaking load (F), elongation at break (ε) and relative strength decrease ($S_{rel.}$) of yarn from enzyme-treated silk fabric samples; * - quantities of other components according to the recipe given in Experimental.*

Composition of bath	F, N	ε, %	$S_{rel.}$, %
untreated yarn sample	2.88	29.3	–
bath without enzyme*	2.81	28.5	2.4
Alcalase 2.5L – 1 %*	2.63	29.2	8.7
Alcalase 2.5L – 1.5 %	2.59	26.7	10.1
Proteopol BP-S-100 – 1.5 %	2.68	27.2	6.9
Proteopol BP-S-100 – 2.5 %	2.66	29.3	7.6

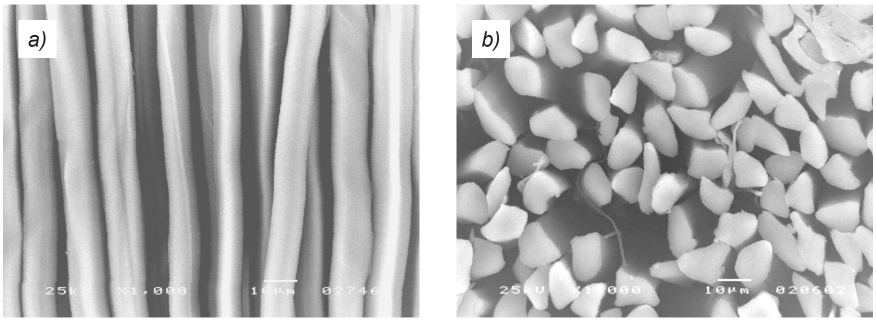

Figure 2. *SEM images of the silk fibres before treatment (magnification 1000 ×); a) fibre surface, b) cross-section of fibres.*

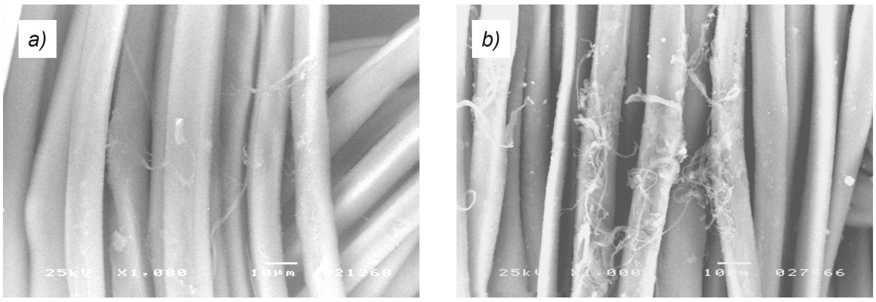

Figure 3. *SEM images of the surface of the silk fibres after enzymatic treatment (magnification 1000 x); a) Proteopol BP-S-100 (2.5%), b) Alcalase 2.5L (1.5%).*

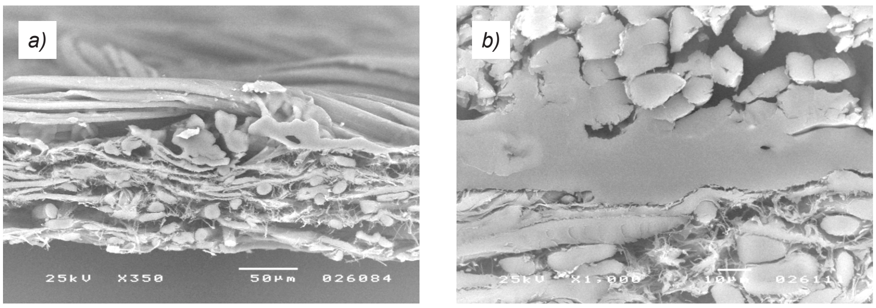

Figure 4. *SEM images of the cross-sections of antique silk fabrics sized onto silk paper (Zamoyski's banner, the second half of the 18 century, Wawel Collections); a) magnification 350×, b) magnification 1000×.*

- changes in the surface structure of silk fibres.

Sheets of *silk paper* with the following compositions were made at the Pulp & Paper Research Institute:

- enzyme-treated silk fibres (65%) + linters (35%),
- unmodified silk fibres (65%) + linters (35%).

The *silk paper* samples, containing modified silk fibres, were used for the conservation of antique silk fabrics, and their basic performance properties were determined.

The conservation operations were carried out at the Academy of Fine Arts in Warsaw.

Results and discussion

Weight loss of fabrics

The weight loss of the silk fabric samples is an indirect measure of enzyme activity. It is also important in terms of excessive fibre strength deterioration. The results of testing the weight loss of the silk fibres under the treatment conditions used (***Figure 1***) can be considered as safe, as they do not exceeding 1.2%. One can clearly observe that Alcalase 2.5L enzyme has greater effects than those of Proteopol BP-S-100.

Tensile strength of silk fibres

The tensile strength was tested using yarn sections taken from enzyme-treated fabrics. The results listed in ***Table 1*** show that treatment with Alcalase 2.5L enzyme results in a higher deterioration of the tensile strength of the silk fibre than that of Proteopol BP-S-100-treated fibres. This is directly connected with the differences in weight loss of the silk fabrics treated with these enzymes.

Changes in the surface structure of silk fibres

The measurements performed by the SEM method show clear changes in the surface structure of silk fibres resulting from the enzymatic treatment. Untreated silk fibres (***Figure 2***) are smooth fibroin threads with a thickness of 12–20 μm. Treatment with Proteopol BP-S-100 enzyme brings about the fibrillation of a few fibres, but it is only barely visible (***Figure 3.a***), while treatment with Alcalase 2.5 L enzyme results in clear changes in the surface of silk fibres (***Figure 3.b***).

Assessment of resulting *silk paper* as conservation material

The enzymatic modification of silk fibres (Alcalase 2.5L – 1.5%) greatly facilitated both the preparation of the cellulose-fibroin pulp and the formation of the silk paper sheets. The tests carried out at the Pulp and Paper Research Institute show that paper containing modified silk fibres is characterised by a 15 - 20% higher tensile strength and clearly higher uniformity than that of paper made from unmodified fibres.

The application tests performed at the Academy of Fine Arts completely confirmed the suitability of the resulting *silk paper* for the conservation of antique silk fabrics. The SEM images of cross-sections of 18th century- silk fabric samples sized together with the *silk paper* (***Figure 4***, see page 115) show a good paper-fabric adhesion. There is no adverse or excessive size penetration into the structure of the reinforced fabrics.

Conclusions

The enzymatic treatment of silk fibres with Alcalase 2.5L enzyme results in clear fibrillation of fibre structure. This change in the surface properties of silk fibres makes it possible to process them by the paper-making method in an aqueous suspension with cellulose fibres and to form thin sheets of *silk paper* containing 65% silk and the remaining 35% made up of linters. The paper obtained, with a basic weight of 20 – 25 g/m^2, shows good mechanical strength and uniformity. The application tests carried out by conservators have shown that *silk paper* is a valuable material for antique fabric conservation.

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