

Conserving Ropes from the Phanom-Surin Shipwreck in Thailand: Case Study on Storage and Exhibition at the National Museum of Thailand

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ABSTRACT

There are several important factors to consider when studying appropriate conservation methods for fibers in museum exhibitions or storage. This research focused on investigating the potential of using Trehalose and polyethylene glycol 4000 (PEG4000) as treatments for shipwreck rope fibers in Thailand's museums. The efficacy of these treatments was evaluated by using a twisted fiber thread to tie the torpedo jar. The initial desalinated fibers were subjected to three groups: untreated rope was dried at room temperature, ropes conserved with Trehalose, and ropes conserved with PEG4000. Identical concentrations of both the Trehalose and PEG4000 solutions started at a concentration of 25 percent brix then increased progressively to 40 percent and 60 percent brix.

We employed four different analyses. We used scanning electron microscopy to study morphological properties. Prior to treatment and after treatment we compared numerical evaluation of the colour change using ΔE^* values (CIE L*a*b* system). We recorded reflectance using wavelengths of white light ranges (380-780 nm). We used differential scanning calorimetry technique for thermal properties.

The results indicate the Trehalose fibers had a melting temperature of 192.8°C and exhibited less change in colour and reflectance compared to the others. The PEG4000 fibers had a melting temperature at 59.3°C. Trehalose had higher thermal properties compared to PEG4000. Thus, Trehalose is an appropriate conservation material for ropes and other fiber-based materials that are stored or displayed in environments with high humidity and temperature, such as the case in Thailand.

Keywords Phanom-Surin Shipwreck, conservation of rope (fiber), Trehalose, PEG4000

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1. INTRODUCTION

The Phanom-Surin shipwreck was discovered at Samut Sakhon, Thailand in September 2013. The shipwreck is dated to the 9th century CE (1stROFAD 2016). We narrow our discussion to the excavated rope fibers. Our literature review on rope fiber or “Tao” fibers identified them as *Arenga pinnata*, commonly known as the sugar palm or Arenga palm (Mahaphol 2013). For centuries sugar palm fibers were used as ropes for ships due to their exceptional strength, durability, and resistance to saltwater (Ishak et al. 2012, 700). Our study expands from this literature review to focus on the conservation of twisted rope/fiber, used to tie Torpedo jars (Figure 2), with a specific emphasis on museum exhibition and storage purposes.

In this study, we compared conservation of fresh sugar palm fibers in PEG4000 and Trehalose, which demonstrated superior properties compared to the non-treated fibers. We examined moisture absorption, which the fibers treated with Trehalose (henceforth Trehalose fiber) showed lower moisture absorption than the fibers treated with PEG4000 (henceforth PEG4000 fiber). We compare the physical characteristics of the fibers that underwent conservation treatment (in either PEG4000 or Trehalose) by the changes in reflectance, colour and heat resistance. Our results are intended for use to design a conservation plan for the appropriate environment for museum display, storage, and conservation.



Figure 1 The twisted fiber used to tie Torpedo jars

2. MATERIALS AND METHODS

2.1 Materials

On the Phanom-Surin shipwreck ropes were used to tie Torpedo jars. PEG4000 ($M_w \approx 3500 - 4000$) was purchased from Loba ChemieTM, India. Trehalose (TREHA[®]) was purchased from Hayashibara Co.Ltd., Japan.

2.2 Samples preparation

We prepared the fiber samples by flushing with deionized water until the electrical conductivity (EC) of the solution was below 100 μ S. The fibers were divided into three groups, dry at room temperature, soaked with Trehalose or PEG4000. We tightly covered the fibers while soaking to prevent water evaporation.

- i. Untreated - The untreated fibers were dried at room temperature.
- ii. Soaked with Trehalose - The fibers were immersed in Trehalose starting with 20 percent brix at room temperature (34°C). The solution was heated, while the Trehalose concentration increased from 40 percent to 60 percent brix. The controlled temperature did not exceed 80°C, and the fibers were immersed for 24 hours. Once the fibers reached the (20, 40, 60) percent brix constants the fibers were dried with an electric-fan until completely dried. The fibers were cleaned with warm water to remove any residual Trehalose and dried until a constant weight is obtained.

- iii. Soaked with PEG4000 - The immersion process in PEG4000 follows the same procedure as immersion in the Trehalose solution, but the fibers were left to dry at room temperature.

2.3 Scanning electron microscopy (SEM)

After sample preparation (see above for details) all fibers were immersed in liquid nitrogen, broken up and stored in a desiccator to absorb moisture for one day. Each were coated with gold (Au-Coating) through an auto fine coater (Smart Coater, DII-29030SCTR) for 4 minutes. Analysis was conducted with a benchtop scanning electron microscope (JCM-7000, JEOL) at 5 kilovolts (kV).

2.4 Differential Scanning Calorimetry (DSC)

After sample preparation and SEM all fibers underwent thermal analysis with the Differential Scanning Calorimetry (DSC) technique (Mettler Toledo brand). Five milligrams (mg) of sample were sealed hermetically in the aluminium crucible. Nitrogen gas was purged at a flow rate of 20 millilitres per minute (mL/min). At a heating rate of 10 °C/min across a range from -20 to 200°C to 50 to 230°C.

2.5 Spectroradiometer

After sample preparation, SEM and DSC all fibers underwent spectroradiometer (Konica Minolta CS-2000), with wavelengths from 380 to 780 nanometers (nm) range. The samples were prepared by twining and thickening the ropes, three random points were selected for spectroradiometer at a 0.2 aperture in the (CIELAB) (Commission Internationale de l'Eclairage, L*, a* and b* represent each of the three values the CIELAB color space uses to measure objective color and calculate color differences. L* represents lightness from black to white on a scale of zero to 100, while a* and b* represent chromaticity with no specific numeric limits. Negative a* corresponds with green, positive a* corresponds with red, negative b* corresponds with blue and positive b* corresponds with yellow). Under the International Commission on Illumination (CIE) commonly used D₆₅ - D series of illuminants portray standard illumination conditions at open-air in different parts of the world - measurements were taken and the reflectance values were averaged. The data was then analyzed for colour variability.

3. RESULTS AND DISCUSSION

Our study focuses on the conservation of waterlogged fiber in Trehalose and PEG4000 that was used to tie Torpedo jars in the Phanom-Surin shipwreck (Figure 2), for the purpose of museum exhibition and storage.

3.1 Scanning Electron Microscopy

Microscopic examinations of fibers treated with Trehalose and PEG4000 show structural differences compared to untreated rope samples. Untreated rope displayed severe degradation, collapse of cells, and the longitudinal section had a hole where the silica had come off (Figure 4-c). Fresh sugar palm fibers retain silica (Figure 7-c). Cross-sections of PEG4000-treated and Trehalose-treated ropes appeared similar to each other. PEG4000-treated rope had a smoother longitudinal surface (Figure 5-c), while Trehalose-treated rope exhibited an orthorhombic crystal form (Figure 6-c). These differences indicate distinct effects of the different immersive treatments of conserved fibers.

Trehalose and PEG4000 conserved fibers of twisted rope show surface cracks due to SEM sample preparation. The micrograph of these twisted fibers (Figure 8) show reduced bend and twist resistance. Specifically, Trehalose exhibits lower twist resistance than PEG4000. In previous research the conserved fibers improved tensile strength (Mahaphol 2013). Trehalose, with its rigid crystalline structure, demonstrates higher tensile strength than PEG4000 and untreated rope.

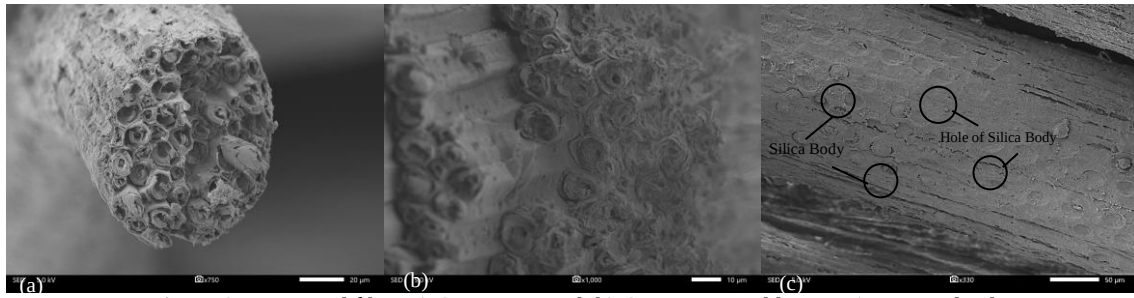


Figure 2. Untreated fiber. a) Cross-sectional, b) Cross-sectional lumen, c) Longitudinal

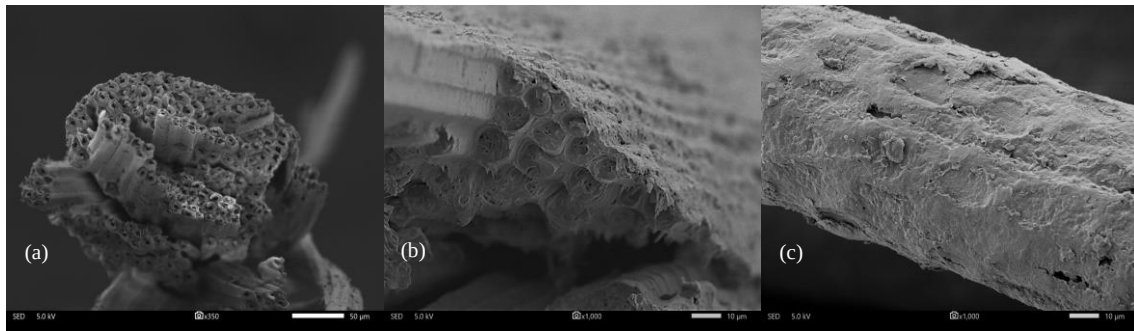


Figure 3. PEG4000 fiber. (a) Cross-sectional, (b) Cross-sectional lumen, (c) Longitudinal

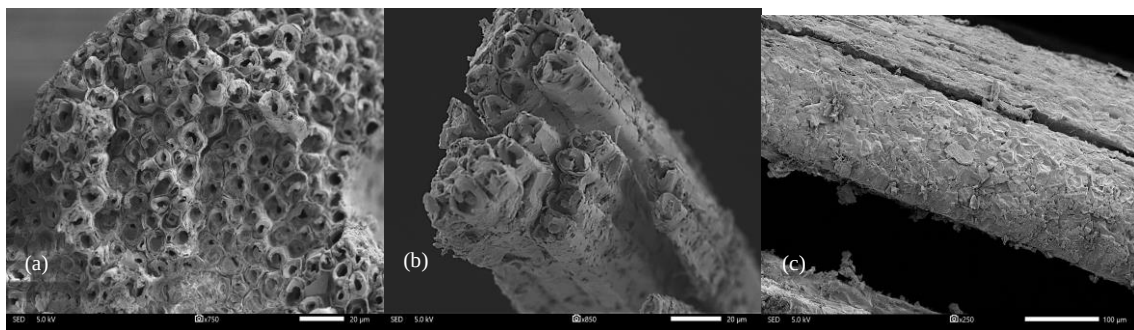


Figure 4. Trehalose fiber. (a) Cross-sectional, (b) Cross-sectional lumen, (c) Longitudinal

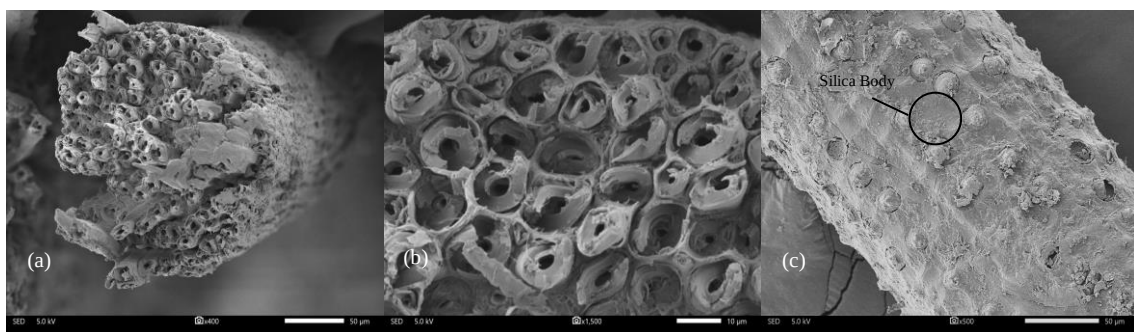


Figure 5. Fresh sugar palm fiber. (a) Cross-sectional, (b) Cross-sectional lumen, (c) Longitudinal

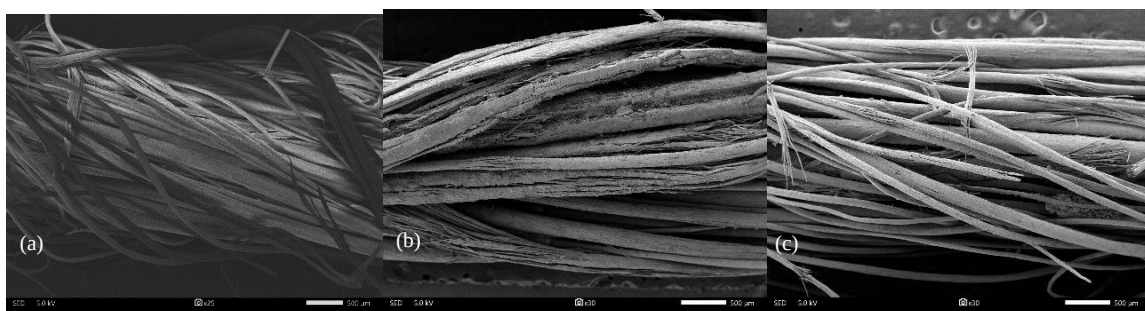


Figure 6. Twisted rope. (a) Untreated rope, (b) Trehalose-treated rope, (c) PEG4000-treated rope

3.2 Reflectance (percent)

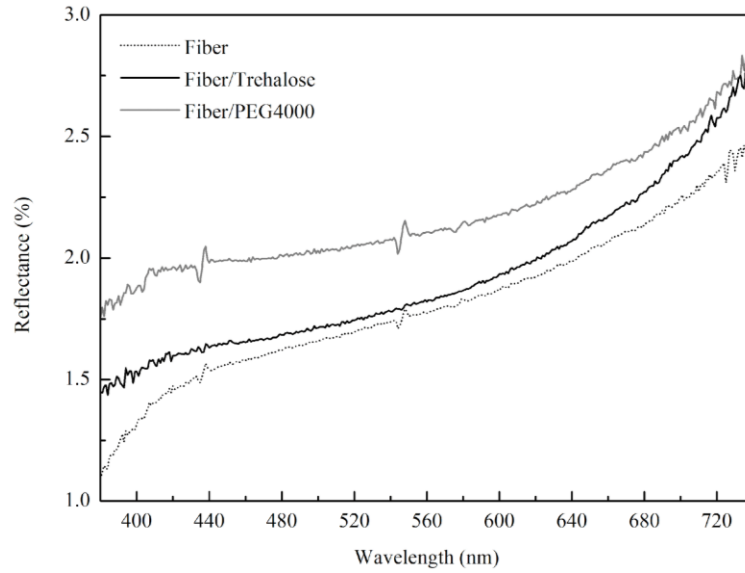


Figure 7. Graph of reflectance comparison results between untreated fiber, Trehalose fiber, and PEG4000 fiber.

The results of the reflectance (percent) measurements indicate that both PEG4000 and Trehalose conserved fibers increased reflectance compared to the non-treated fiber. Pointedly, the PEG4000 fiber exhibited higher reflectance percentage than the Trehalose fiber. This suggests that PEG4000 treatment may have more significant impact on enhancing the fiber's reflective properties. PEG4000 fiber (Figure 5-c) surfaces were coated with a layer of silica so the longitudinal surface reflection was smoother and more uniform, which resulted in regular reflection of incident light. In contrast, the Trehalose fiber (Figure 6-c) have rough surfaces with irregularly shaped rectangular features and thickness varies, which leads to scattered reflection of incident light. The diffused light in multiple directions is disordered and does not exhibit regular reflection. This causes a decrease in the detected signal.

3.3 Colour measurement ΔE^*

Table 1 shows the results of the $L^*a^*b^*$ colour space data for untreated fiber, Trehalose fiber, and PEG4000 fiber.

Treatment	$L^* \pm SD$	$a^* \pm SD$	$b^* \pm SD$	ΔE^*
No-treatment (PSF ^a)	14.17±2.20	0.66±0.21	2.20±0.23	-
PSF/PEG4000	15.85±3.05	0.56±0.77	1.03±0.44	2.05
PSF/Trehalose	14.12±4.49	0.98±0.53	2.03±0.98	0.37
No-treatment (Currently)	23.53±4.59	1.89±0.60	7.33±0.45	10.74

Note: ^a PSF refers to Phanom-Surin fiber

The untreated fiber has a low L^* value of 14.17, indicating a relatively dark colour. The positive a^* value of 0.66 and positive b^* value of 2.20 suggests the colour of the untreated fiber has a slightly reddish-yellow hue. The PEG4000 fiber increased the L^* value to 15.85, indicating a brighter colour. The a^* value decreased slightly to 0.56, indicating a slightly greener hue, while the b^* value decreased significantly to 1.03, indicating a more blueish hue. The Trehalose fiber resulted in a similar L^* value as the untreated fiber at 14.12, but a higher positive a^* value of 0.98 and a higher positive b^* value of 2.03. This suggests that the Trehalose fiber colour has a more reddish-yellow hue than the untreated fiber.

The CIE $L^*a^*b^*$ colour system allowed us to evaluate the colour change of the fiber. The colour difference (ΔE^*) was calculated by comparing the colour values of the treated and non-treated fibers. ΔE^* value greater than one was considered visually detectable.

The results of the colour measurement ΔE^* for PEG4000 fiber (2.05) and Trehalose fiber (0.37) (non-treated fiber so there is no ΔE^* value) indicate that the addition of PEG4000 to the fiber caused a significant colour change, while Trehalose fiber minimally changed. These findings suggest that the Trehalose treatment more effectively preserves the colour stability of the sugar palm fiber than PEG4000. The cause of colour change requires further investigation.

3.4 Differential Scanning Calorimetry (DSC)

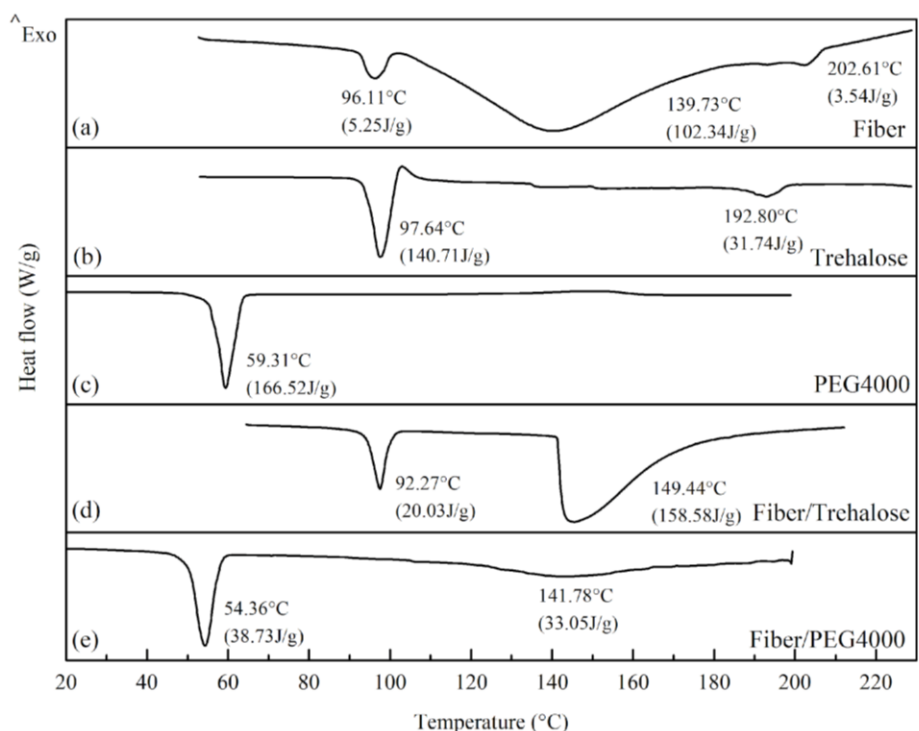


Figure 8. DSC thermogram of untreated fibers (a), pure Trehalose (b), pure PEG4000 (c), Trehalose fibers (d), and PEG4000 fibers (e): 1st Heating.

We investigated the thermal properties of fibers following preservation with Trehalose and PEG4000 treatment, which resulted in changes in the thermogram characteristics of the fibers.

Figure 10 (a) and (d) show the relationship between Fiber and Fiber/Trehalose. DSC thermogram: peaks at 96.11°C and 139.73°C for Fiber, and 92.27°C and 149.44°C for Fiber/Trehalose. The first peak corresponds to water evaporation. Fiber/Trehalose has more easily evaporated water due to the attributed hydroxyl groups in the cellulose structure, which make it difficult to bond with water. The presence of a hydroxyl group of Trehalose in Fiber/Trehalose also binds to the cellulose of the fiber, causing a decrease in the amount of bonding between water and cellulose. At 149.44°C, the melting temperature (T_m) of Fiber or Fiber/Trehalose occurs. In fact, Trehalose's melting temperature is at 192.80°C, which causes the crystals of the Trehalose chain to fold into lamellae this absorbs heat energy from surroundings and causes vibrations until the intermolecular attraction is overcome. As a result, the crystals dissociate into randomly spaced Trehalose chain molecules. The second peak of Fiber/Trehalose (Figure 10 (b)) covers Trehalose's melting peak and has a wide range. The temperature transition from glassy state to rubbery state (T_g) occurs at 106.50 °C, where Trehalose chains in the amorphous region absorb heat energy, which increase distance between chains and free up space for volume. Comparison of the DSC of Fiber and Fiber/Trehalose, Trehalose treatment raised the second peak temperature, this indicates higher melting temperature and improved high-temperature resistance.

Figure 10 (a) and (c) show the relationship between Fiber and Fiber/ PEG4000. From and (c), the first peak observed at 54.36°C (Figure 10e) corresponds to the melting temperature (T_m) of PEG4000. A lower melting point than Trehalose. PEG4000 is composed of repeated units of ethylene glycol, which

enable it to form hydrogen bonds with water molecules. In comparison, Trehalose is composed of a cyclic glucose disaccharide that forms strong hydrogen bonds due to the two glucose molecules being linked by an α,α -1,1-glycosidic bond. These structures when compared result in Trehalose's higher melting temperature than PEG4000.

Based on the thermal investigation, Trehalose-treated rope showed superior thermal stability and less moisture absorption than PEG4000.

4. CONCLUSION

We demonstrated the use of Trehalose and PEG4000 in the conservation of twisted fiber used to tie the torpedo jars on the Phanom-Surin shipwreck. The results showed the Trehalose fibers had less change in colour, reflectance and higher thermal properties compared to the PEG4000 fibers. We conclude Trehalose is an effective conservation material for fibers in high humidity and temperature environments. The use of Trehalose as a conservation treatment for sugar palm fibers created a barrier between the cellulose structure and water, which reduced the amount of water that can evaporate from the fibers. The experiments in this study are informative and favour Trehalose as the preferred fiber treatment for museum display and storage in high humidity and heat environments, such as Thailand.

Acknowledgements

The authors sincerely thank Mr.Sanae Mahaphol and Ms.Sopit Panyakhan, Scientists from conservation science division, and The Fine Arts Department of Thailand for their help and constant encouragement. Thanks Ms.Sirin Yuanyaidee, Director of Kanchanaphisek National Museum and staff. Thank you Assoc.Prof.Dr.Mantana Opaprakasit and Dr.Intatch Hongrattavichit from Faculty of Science Chulalongkorn University for their support with the analysis instruments and their advice. Moreover, we're grateful to the Sumitomo Foundation, Japan and Ms.Umaporn Kruekamwang, Director of Office of National Science Museum Thailand for the support.

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