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Is it safe to irradiate historic silk textile against fungi?

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ABSTRACT

The finding of heavily damaged historic silks prompted this study to answer the title question on possible unwanted effects of fungal decontamination by gamma-irradiation. Although silk fiber constitutes of relatively stable protein fibroin heritage silk textiles need protection from biodegradation. Low-dose (0.5 – 2 kGy) gamma-irradiation is already recognized as a fast, temperature independent method of insect eradication. For fungal decontamination, somewhat higher absorbed doses are needed. Since possible unwanted side effects to already damaged material must be excluded, model samples were prepared by aging contemporary silk. Some of the unaged and aged samples were irradiated to 6 kGy and other to a much higher dose of 120 kGy to identify radiation-specific damage, if any. In order to achieve detectable damage selected irradiated and non-irradiated model samples were subjected to further artificial aging. None of the assessment methods used (ATR-FTIR, SEM thermal analysis) revealed any radiation-specific change. Provided that the fibroin conformations are identified and analyzed separately, FTIR is the method of choice for monitoring the effects caused by any treatment of silk. An increase in the amide I/II absorption intensity ratio is a sensitive though ambiguous indicator of silk degradation. Transformation of more stable beta-sheet to alpha/random coil fibroin conformation is a definite proof of degradation. It occurred exclusively on artificial aging of model silks and was accompanied by pronounced morphology changes confirming the role of conformation on silk stability. In non-treated historic silks the fraction of more stable beta-sheet conformation was unexpectedly high as was the iron content that likely protected silk structure. Since irradiation produced insignificant and likely partially reversible effects radiation treatment of silk textile is deemed safe beyond the absorbed dose proposed as an upper limit for fungal decontamination, 8 ± 2 kGy.

1. Introduction

Cellulose and some proteins are main natural polymers that constitute cultural heritage objects prone to biodegradation. Silk is one of the most commonly used natural textile fibers. Raw silk consists of two proteins, fibroin, that is, the fiber, and sericin, a "glue" that binds and protects fibroin filaments. In the production of silk textile sericin is washed away in a process called degumming. Silk is relatively stable textile so it is common in heritage collections and archaelogical findings. However, molds and fungi attacks occur everywhere including the store rooms of museums and collections (Tiano, 2002; Szostak-Kotowa, 2004; Sterflinger et al., 2010). The contamination of objects outside the museums and particularly those found in the excavations can be much worse and even endanger the health of personnel handling such objects (Katušin-Ražem et al., 2017a, 2017b). In order to reduce the bio-burden and extend the lifespan of heritage objects treatments by various methods like fumigation (exposition to toxic gases), anoxia (removal of oxygen by introducing the inert gases) and biocides are applied. The effects of all these methods are diffusion-limited and most of them have serious side-effects to the material of treated object and to the environment. The enzymes that fungi produce can continue to degrade the object even after the initial attack has been treated (Chu et al., 2011; El-Tablawy et al., 2014).

Gamma-radiation is highly penetrating form of ionizing radiation that treats the objects throughout the entire volume. Ionizing radiation permanently damages DNA molecules of biodegrading agents (insects, fungi and molds, bacteria) (Ražem, 2004; Katušin-Ražem et al., 2017a, 2017b) and at least partially inactivates their enzymes (Chu et al., 2011). Radiation treatment is fast, temperature independent, leaves no residues, and does not induce radioactivity. The objects may be irradiated packed and remain protected while the packaging is intact. Although irradiation effects depend on a single parameter, an absorbed

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dose, *D*, appropriately irradiating a heritage object may be challenging. The dose has to be large enough to efficiently reduce bio-burden but not to damage the object in any way. The radiation sensitivity of the biodegrading agents that is known from radiation sterilization and sanitation (Ražem, 2004) is a primary factor in selection of an adequate absorbed dose. Restorers and conservators dealing with textile protection are particularly concerned of side effects of any treatment to the point that they sometimes deliberately choose to do nothing. To comply with the high standards of the restoration profession, the protection against unwanted side effects to the materials that have mostly already been damaged is a high priority. Because of that, the goal is to reduce fungal population to an acceptable level, not to achieve full sterility. Consequently, an absorbed dose in the range of 2–10 kGy is deemed adequate (Magaudda, 2004). The absorbed dose of 8 ± 2 kGy was recently proposed as maximum absorbed dose to be applied in heritage treatment of fungal population (Ponta et al., 2017). Protease activity of some very common *Aspergillus* molds will simultaneously be reduced since El-Tablawy and Araby (2014) showed that doses of 4 and 6 kGy produced that effect. That is particularly important for protein based textiles like silk. However, a dose of 10 kGy sometimes may not be enough. In cases of heavy contamination or inadequate conditions the object has been kept in, it may be necessary to apply significantly higher doses up to 25 kGy and/or repeated irradiation so that the quantity of fungi decreases to the acceptable level. (Katušin et al., 2017b; Rizzo et al., 2002). On the other hand, the material(s) constituting the object may be sensitive and/or heavily damaged so the absorbed dose needs to be reduced. Because of that, the irradiation must be done only by an experienced team at an appropriate facility (Ponta et al., 2017). The absorbed dose must be fine tuned depending on the type and state of all the materials that constitute the object in each particular case. The final decision on the appropriate absorbed dose has to be made by irradiation facility staff in cooperation with restorers and other specialists knowledgeable on the response of aged materials to gamma-radiation.

On an incidental finding of heavily damaged remnants of silk clothing dating from approximately 17th century AD in a crypt of the Dominican Monastery in Ptuj, Slovenia, the curators of Ptuj Museum decided to treat bio-burden with gamma-radiation at the irradiation facility of the Radiation Chemistry and Dosimetry Laboratory (RCDL) of the Ruđer Bošković Institute (RBI) in Zagreb, Croatia. Irradiation of various cultural heritage objects has been carried out there for 30 years. In that period more than 8000 objects made of various perishable materials were successfully treated and significant experience gathered (Ražem, 2004; Katušin-Ražem et al., 2009, 2017a, 2017b). However, textiles were treated infrequently so we needed to find out whether the radiation treatment of heritage silk textile to doses needed for decontamination of fungi is safe. The available literature was not helpful since it mainly deals with radiation effects on fibroin films (for example Xiong et al., 2011). A number of authors (Yanagi et al., 2000; Pewlong et al., 2003; Kojthung et al., 2008) studied irradiation of silk to very high absorbed doses, much higher than that needed for treatment of fungi. Because of that we used modern silk textile as a model and part of it subjected to artificial aging treatment to make it similar to historic one and then irradiated to a typical absorbed dose for a fungal treatment. Additionally, a much higher dose was applied to another part of samples to see if there will be any change caused exclusively by gamma-irradiation. Selected non-aged and aged irradiated samples were subjected to post-irradiation aging to provoke maximal degradation and ensure that its effects were correctly identified. The suitability of some of the most common experimental techniques for characterization of polymers that occur in heritage textiles (ATR-FTIR spectroscopy, scanning electronic microscopy and thermal analysis) was also tested.

Table 1
List of sample labels indicating absorbed doses of gamma-radiation and aging treatments, if any. (***A1*** stands for artificial aging before while ***A2*** indicates artificial aging after the gamma-irradiation).

Contemporary silk samples	Not aged prior to irradiation	Aged prior to irradiation
Not irradiated	***control***	***A1 control***
D = 6 kGy	***6 kGy***	***A1 6 kGy***
	6 kGy A2	***A1 6 kGy A2***
D = 120 kGy	***120 kGy***	***A1 120 kGy***
	120 kGy A2	***A1 120 kGy A2***
historic silk samples		
Not irradiated	***Arch Silk 1***	
	Arch Silk 2	
D = 4 kGy	***Arch Silk 4 kGy***	
D = 6 kGy	***Arch Silk 6 kGy***	

2. Materials and methods

2.1. Samples

A commercial degummed contemporary silk fabric (pongé, 32 g/m^2) was used for model samples. Historic silk samples were remnants of different garments dating from approximately 17th century AD found in a crypt of the Dominican Monastery in Ptuj, Slovenia. All historic samples were brown and some silk lustre was still present. The samples were cleaned by brushing. Because of the location where the silks were found, the pre-irradiation microbiological testing was necessary. It revealed relatively low and benign biological contamination. Two fungal taxa were recovered: a strain belonging to *Aspergillus niger* species complex, and hitherto unidentified *Penicillium sp*. Beside fungi, bacteria belonging to a single species *Bacillus cereus* were isolated.

All sample labels are listed in Table 1. An indication of the treatment applied to the samples is included as well.

2.2. Gamma-irradiation conditions and artificial aging regimes

Since very limited quantity of historic silk was available, the artificial aging experiments were done exclusively on model contemporary silk samples. Two artificial aging regimes were devised to which selected silk samples were subjected before the gamma-irradiation (***A1***), after it (***A2***) or in both cases. ***A1*** treatment was photo-aging by exposure to light spectrum similar to that of the sunlight for 14 days in a chamber with metal-halide bulb. Average density of the light was 100 W m^{-2} and the temperature of the white body was 40 °C. Total energy of photo-irradiation was 33.6 kW h m^{-2}. The artificial aging ***A2*** consisted of thermal and photo-aging for 14 days each. Firstly, thermal aging was performed in a hygro-thermal chamber where the temperature and relative humidity (RH) were stepwise cycled;each step lasted for 30 min. In the first and third step temperature was t = 25 °C and RH = 50%, in the second step temperature was t = 50 °C and RH = 90% whereas in the fourth step temperature was t = 0 °C. The subsequent photo-aging process was identical to previously described. A non-aged and another aged but non-irradiated samples were kept as controls (***control*** and ***A1 control***).

Gamma-irradiation was performed in ambient conditions in a panoramic ^{60}Co gamma-source at Radiation Chemistry and Dosimetry Laboratory, Department for Materials Chemistry Ruđer Bošković Institute. The dose rate of 10 kGy h^{-1} was established based on the measurements of an absorbed dose using the ethanol-chlorobenzene dosimeter (Ražem et al., 1985). Model contemporary silk samples were irradiated to 6 kGy and 120 kGy respectively while the historic silks were exposed to lower absorbed doses of 4 kGy and 6 kGy. All the silk samples were kept in dry conditions.