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Insight into the measurements for determining the ageing degree of ancient silk



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1. Introduction

Silk which produced and excreted by silkworm is a natural material that has been used for over 5000 years [1,2] to produce numerous precious textiles and other artifacts [3]. Silk fibre is a polymer composed of sericin and fibroin, which are two types of proteins consisting of C, H, O, N etc. [4]. Before weaving, raw silk is normally subjected to a degumming process in which the majority of silk sericin has been removed [4,5]. And the degummed silk contains mainly fibroin which composed of amino acids (mainly alanine, serine, glycine and tyrosine) that fold into antiparallel β sheets crystallites and an amorphous region [6]. Two subunits constitute the amorphous region of silk fibroin are the heavy chain and the light chain. The heavy chain was identified with twelve hydrophobic domains mainly contain (GAGAGS)_n amino acid sequences which ensures the heavy chain's resistance to the degradation factors, such as moisture, heat, UV radiation, acidity or alkalinity etc. [7,8,9]. On the other hand, the light chain which linked to the heavy chain by disulfide bonds is an independent sub-unit that exhibits less stability and would degrade prior to the heavy chain [9]. The unique structure makes silk one of the most sensitive natural fibers that is easily influenced by common deteriora-

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ABSTRACT

Evaluating the degradation degree of aged silk is a challenge but worthwhile to determine the structure change and stability of silk. To date, the characterizations of silk degradation are widely studied, however, it still remains a lack of systematic research on measuring and quantifying the degradation degree of silk with effective ageing indicators. In this research, ancient silk samples from two different ages and regions were investigated by means of X-ray diffraction, X-ray photoelectron spectroscopy, EPR spectroscopy and ¹³C CPMAS NMR in an attempt to provide numerical indicators for assessing their ageing degree. As a result, the crystallinity, oxidation and carbonization degree, variation of amino acid content and content of random coil were proved to be the valuable indexes for interpreting the distinct deterioration and fragility level of aged silk. This work may shed light on studying the ageing status and stability of historical silk and further providing evidence for the conservation and preservation of silk cultural relics.

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tion agents. As a result, only a small amount of silk-based cultural relics has survived after long-time burial and most of them are not with their original appearance. It is of great importance to prevent these precious treasures from further deterioration. Therefore, the fundamental work is to investigate the degradation of ancient silk by assessing the degree of ageing and evaluating the stability.

To date, the characterizations of silk degradation are widely studied. The focus shifts from morphological level to molecular level of silk by employing various methods, such as Fourier Transform infrared spectroscopy (FT-IR) [3,10–15], X-ray diffraction (XRD) [16–19], amino acid analysis [5,20,21] and electron paramagnetic resonance (EPR) spectroscopy [4]. However, most of the reported works focused mainly on evaluating the property changes upon the variation of structure and composition of silk. There still remains a lack of systematic research on measuring and quantifying the degradation degree of silk with effective ageing indicators, in order to accurately determine and further compare the deterioration status of ancient silks.

The crystallinity of silk protein is proved to be an important indicator that reflects the ageing of silk [19], where XRD offers a direct and accurate method to quantitatively study the crystallinity of silk. Besides, XPS is a powerful element analytical tool for characterizing the chemical bonding states of elements in near-surface regions of a solid compound up to the depths of about 10 nm [22]. The elemental composition of silk surface along with the chemical state which was obtained by employing XPS analysis can be an-



Fig. 1. ancient silk samples (a. BM; b. FM) and modern silk sample (c. MS).



Fig. 2. SEM images of ancient silk samples BM (a,b) and FM (c,d), and modern silk sample MS (e,f); and SEM-EDS spectrogram of BM (g) and FM (h).



Fig. 3. Deconvolution of XRD pattern of MS, FM and BM (a-c, black solid curve represents original spectra; red solid curve represents simulated spectra from summed peaks; other solid curves represent decomposed components), and plots of crystallinity derived from deconvolution of XRD patterns (d).

other indicator to characterize the deterioration of silk. EPR was applied in determining the free radicals which is believed to take part in the degradation process of ancient silk fabrics [4]. On this basis, the index of carbonization of silk is proposed by measuring the accumulation of carbon radicals [23]. And the content of amino acid is confirmed to be another valuable indicator of ageing level of silk [5]. In addition to the commonly used amino acid analysis, ¹³C CPMAS NMR could be a better solution for estimating the content of amino acid and further revealing the intensity ratio of β -sheet and random-coil peaks of silk.

In this paper, the degradation behaviors of two ancient silk textiles from different regions with increasing burial time from the Southern Song Dynasty (1127–1279 A.D.) to the Warring States (403–221 BC.) were investigated in comparison with the modern silk. XRD, X-ray photoelectron spectroscopy (XPS), EPR and ¹³C Cross Polarization Magic Angle Spinning Nuclear Magnetic Resonance (¹³C CPMAS NMR) were employed to measure the crystallinity, oxidation and carbonization degree, variation of amino acid content and content of random coil. The results and findings provided numerical ageing indicators for interpreting the deterioration status of ancient silk. The research would be beneficial to determine the structure change and stability of silk, and further provide scientific evidence for the conservation of ancient silk.

2. Materials and methods

2.1. Historical and modern silk textiles

The two ancient samples (see Fig s.1a and b) studied are the silk debris unearthed from Baling Mountain, Jingzhou, Hubei Province



Fig. 4. XPS survey spectra of BM (a), FM (b) and MS (c).

Table 1

Relative chemical composition and atomic ratio determined by XPS for the ancient samples and modern sample.

Samples	Chemical co	Chemical composition/%			Relative area of different chemical bonds (%)			Atomic ratio	
	C1s	01s	N1s	C-C	C-N/C-O	C=0	O/C	N/C	
BM	53.33	38.36	8.31	27.51	16.19	9.63	0.72	0.16	
FM	62.36	27.03	10.61	34.34	16.31	11.71	0.43	0.17	
MS	63.95	21.6	14.46	30.98	18.33	14.64	0.34	0.23	



Fig. 5. EPR spectra of samples BM, FM and MS (amplification normalized).

and Fangmao Mountain, Changzhou, Jiangsu Province, denoted respectively by BM (Baling Mountain) and FM (Fangmao Mountain). BM was traced back to the Warring States (403–221 BC.) while FM was dated to the Southern Song Dynasty (1127–1279 A.D.). Commercial silk fabric (denoted by MS, see Fig. 1c) from Guanghua Silk Co. Ltd. of Hefei City was purchased and used as control sample.

One piece with approximately 20 mg was collected from the ancient samples and the fresh silk respectively. The ancient silk pieces were rinsed by using deionized water to remove possible contamination and dried at room temperature. To avoid possible interference of pollutants and deviation caused by uneven ageing of the fibers, the silk samples were further grinded into powder for XRD, XPS, EPR and ¹³C CPMAS NMR examinations.

2.2. Scanning electron microscopy (SEM)

Silk samples were mounted onto a double-sided adhesive carbon tape set on aluminium stubs, which were spatter coated with gold for electric conduction. SEM-EDS analysis was carried out with a ZEISS GeminiSEM 500 scanning electron microscope to characterize the morphology and determine the major elements.

2.3. Wide angle X-ray diffraction

XRD measurements were performed on the modern and ancient samples using a D/max-TTRIII instrument with Cu Ka radiation (λ = 0.1542 nm). The scanning speed was set at 8°/min over a range of 5–35°. The XRD pattern was obtained by using Grams/AI 9.2 software. And the crystallinity of silk was determined by applying Gaussian band shapes. The degree of crystallinity was calculated by using the following equation (eq. 1) [23]

$$\chi_{\rm c} = \frac{I_{\rm c}}{I_{\rm c} + I_{\rm a}} \times 100\%$$

Where Ic and Ia represents respectively the sum of the integrated intensity of the Bragg peaks (200 and 210) and the integrated intensity of the amorphous halo.

2.4. X-ray photoelectron spectroscopy

The chemical compositions of samples were determined by using X-ray photoelectron spectroscopy (Thermo Escalab 250Xi, Thermo Fisher Scientific, USA) with an Al Ka X-ray source (hv = 1486.6 eV). The measurement started with a survey scan from 0 to 1200 eV. X-ray beam spot was 300 μ m \times 700 μ m. For obtaining the relative atomic concentrations of C1s, O1s, N1s, a high resolution analysis was then conducted.

2.5. EPR

The EPR spectra were taken on a JEOL JES-FA200 EPR spectrometer at room temperature with the following parameters: microwave frequency of 9.06 GHz, microwave power of 0.998 mW and modulation amplitude of 0.35 mT.

The degree of carbonization (DC) was calculated by applying the following equation (eq. 2) [24],

$$DC = \ln\left(\frac{30H_0}{\alpha_0 m_0}\right)$$

 H_0 indicates the peak height, and α_0 and m_0 represent respectively the magnification of EPR and applied sample size (samples of 10.0 mg were employed in the test).

2.6. ¹³C CPMAS NMR

The ¹³C CPMAS NMR analyses were carried out using a Bruker AVANCE NEO 600 spectrometer operating at 600.16 MHz on proton and 150.92 MHz on carbon, equipped with a 3.2 mm CPMAS probe. The samples were packed and spun at the magic angle spinning rate of 22 kHz. All the spectra were acquired at temperature of 293 K by using cross-polarization pulse sequence. The 90° pulse was 2.6 μ s with a contact time of 3 ms. Cross-polarization spectra were recorded acquiring 2048 scans to obtain a good signal-tonoise ratio.

3. Results and discussion

3.1. Morphological comparison

SEM is widely used to observe the fibre morphology in order to characterize the degradation of ancient silk. As shown in Fig. 2ef, the modern silk is well-preserved and presents shiny and flexible fibers. In comparison, samples BM and FM (in Fig. 2a-d) were

Table 2° of carbonization of BM, FM and MS.

Samples	H ₀	α ₀	Degree of carbonization
BM	7171.8	300	4.27
FM	6216.9	600	3.44
MS	1192.1	300	2.48



Fig. 6. ¹³C solid state NMR spectra and responding attributions of MS (a), FM (b) and BM (c).

severely damaged that exhibiting fibre fracture and mass contaminations. Amongst them, the deterioration of BM seems much more serious since the surface of the fabric is predominated by longitudinal cracks and fibrillation. SEM-EDS results (in Fig. 2g-h) indicated the particles spread over the surface of BM and FM contain mainly Al and Si. It is speculated that these inorganic pollutants should be the alumina and silica from the burial soil. Therefore, prior to any further examination, the aged silk samples went through a rinsing process to remove possible contamination.

3.2. Crystallinity

The deconvolution XRD patterns of MS, FM and BM were shown in Fig. 3a-c. There were five Bragg peaks for β -sheet crystallites and a board amorphous halo presented in the XRD pattern of MS that arise from the small size of the crystallites. The Bragg reflection at (210), (200) and (002) indicate the crystallite size along \vec{a} (inter-chain direction), \vec{b} (inter-sheet direction) and \vec{c} (fibre axis direction) axes. The band positions along with the crystal size of \vec{a} , \vec{b} , \vec{c} direction is basically in accordance with the previous study [19]. The crystallinity of modern silk fabrics is calculated to be around 45%. In comparison, three Bragg peaks for β -sheet crystallites and a broad amorphous halo were identified in both the XRD pattern of FM and BM, where the crystal planes (002) and (300) disappeared due to the degradation of ancient silk. The crystallinity of FM increased to 50.4% while the crystallinity of BM jumped to 69.1% (diagram presenting the variation of crystallinity is given in Fig. 3d).

3.3. XPS analysis

The distinct chemical compositions of aged silks and fresh silk were measured by XPS. Based on chemical shifts caused by changes in the binding energy of different inner electrons in the chemical environment of atoms, XPS can be applied to determine the oxidation state. Generally, oxidative degradation is the main cause of the degradation of polymer material. By measuring the atomic percentages of C, N and O elements as well as the O/C value, the degree of oxidative degradation of silk can be inferred. The change of N/C value reflects the change of N-containing functional groups within the silk fibre structure. The binding mode and state of C element determine the structure and properties of silk protein in major ways. The high-resolution fine scanning of C1s was performed to acquire the valuable information in the study of the chemical composition of silk fibre.

In Fig. 4, the presence of C1s (286.0 eV), O1s (532.0 eV) and N1s (400.0 eV) were found in the full range XPS survey where the variation of the relative intensity of C1s, O1s and N1s peaks were noted. As listed in Table 1, the contents of C decreased from 63.95% (in MS) to 62.36% (in FM) and 53.33% (in BM) where the contents of O increased in both BM (38.36%) and FM (27.03%) comparing to that of MS (21.6%) which overall resulted in an upward trend of O/C atomic ratio in ancient samples. It is suggested that the historic silks have undergone different degrees of oxidative degradation with the reduction of non-oxidized carbon content upon ageing. Moreover, the contents of N reduced from 14.46% (in MS) to 10.61% (in FM) and 8.31% (in BM) while N/C values and C-N/C-O and C=O bond contents declined in the same way which indicates the breakage of peptide bonds in the main chain of the ancient silk fibers or the lack of N-containing functional groups in the side chain, such as tryptophan, proline, histidine etc.

3.4. Degree of carbonization

As seen in Fig. 5, all the EPR spectra have the similar resolved characteristic absorption peak centred at the highly isotropic g-factor of 2.0037 without hyperfine structure, indicating that the signals were originated from the carbon radicals [4]. Some corresponding features herein are almost identical to those obtained from coal excluding the highly isotropic $gw\sim 2.0037$, the peak-to-trough width of ~ 1 mT and the slightly asymmetric spectral shape [25]. The peak height of EPR signal directly associates with the content of carbon radicals. Therefore, the degree of carbonization of silk can be represented by the derived concentration of carbon radicals [24]. By applying eq. 2, the values of DC were calculated to be 4.27 of BM, 3.44 of FM and 2.48 of MS, as summarized in Table 2.

3.5. ¹³C CPMAS NMR analysis

¹³C CPMAS NMR spectroscopy was carried out to analyse the secondary structure of the fibroin molecule of silk. The spectrum

Table 3

"C chemical shifts and corresponding attribu	tions.
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Peaks no. as	Functional	Corresponding	Chemical shifts δ (ppm)			
marked in Fig. 6	groups	amino acids	MS	FM	BM	
1	CO	Ala	172.74	172.76	172.77	
2	CO	Gly	169.43	169.42	169.45	
3	Cζ	Tyr	155.69	155.47	155.61	
4	Cγ	Tyr	130.78	130.61	130.83	
5	C_{δ}	Tyr	127.67	127.39	128.37	
6	C_{ε}	Tyr	115.72	115.65	115.60	
7	C_{β}	Ser	63.65	64.44	64.59	
8	Cα	Ser	55.42	54.97	54.74	
9	Cα	Ala	49.43	49.34	49.36	
10	Cα	Gly	43.15	43.06	43.05	
11	C_{β}	Ala	20.31	20.76	20.62	

of samples BM, FM and MS are shown in Fig. 6 along with the 13 C chemical shifts and corresponding attributions listed in Table 3.

Fibroin is predominated by glycine (Gly), alanine (Ala), serine (Ser) and tyrosine (Tyr) [5]. As presented in Table 3, peaks denoted by no.2 and 10 are assigned to carbons of Gly, while peaks no.1, 9 and 11 are attributed to carbons of Ala. Where peak no.7 is associated with Ser-C_{β} and peaks no.3–6 belong to carbons of Tyr. Obviously, these peaks appeared at the very similar positions in both ancient silks and fresh silk.

Fig. 7 shows the relative contents of Gly, Ala, Ser-and Tyr-that acquired through spectra fitting of Gly-C α , Ala-C α , Ser-C $_{\beta}$ and Tyr-C $_{\zeta}$ peaks (due to the overlapping of carbonyl resonance regions at 180ppm-165 ppm and Tyr-C α and Ser-C α peaks at 55 ppm as a result of the close chemical shift and background noise of Tyr-C $_{\beta}$ peak at around 35 ppm, these peaks were not considered in spectra fitting). Besides the slightly higher content of Gly, the analytical results for the amino acids of fresh silk are consistent with previous literature reports [26–28]. As seen from Fig. 7, the contents of Gly-and Ala-show non-significant variation in both modern sample and ancient samples while Ser-and Tyr-present obvious lower



Fig. 7. the relative contents of Gly, Ala, Ser-and Tyr-in MS (a), FM (b) and BM (c).



Fig. 8. Spectra fitting of ¹³C CPMAS NMR Ala-C_{β} for MS (a), FM (b) and BM (c).

contents in aged silks then that of fresh silk. It can be explained by the fact that Gly-and Ala-with uncomplicate side chain conformation are stable and predominately locate in crystalline region where Tyr-with long side chains exists mainly in non-crystalline region and is chemically active [29].

¹³C solid state NMR spectra of three samples exhibit asymmetrical broad peaks of Ala- C_{β} which reflect distinctive molecular conformation of silk fibroin. Hence the relative contents of silk secondary structure can be determined by spectra fitting of Ala- C_{β} peaks. As shown in Fig. 8, the shapes of Ala- C_{β} peaks of aged samples present significant variation in comparison with the modern sample. The fitting results (listed in Table 4) reveal that the contents of β -sheet in BM, FM and MS are respectively 85.62%, 77.46% and 70.77%. It is entirely consistent with the mechanism that the amorphous region is degraded prior to the crystalline region during the deterioration of silk [9].

4. Discussion

SEM is an effective tool in providing information on the morphology degradation of silk. Normally, the ageing traits can be distinguished by observing the silk fibre form. By comparing the SEM Table 4

Ala	$a-C_{\beta}$	chemical	shifts	and	relative	contents	of	second	lary	structure.	
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	β -sheet		Random coil			
	Chemical shifts (ppm)	Percentage (%)	Chemical shifts (ppm)	Percentage (%)		
MS	20.38, 22.76	70.77	17.09	29.23		
FM	20.57, 23.04	77.46	16.67	22.54		
BM	20.34, 22.72	85.62	17.25	14.38		

images of BM, FM and MS, it is obvious that MS is in good preservation while FM presents ageing characteristics and BM degraded even more serious. However, it is insufficient for SEM to accurately measure the degradation degree of these silks and offering numerical results for interpreting their deterioration status. Hence, systematic research on measuring and quantifying the degradation degree of silk with effective ageing indicators is desired.

The crystallinity can be a convictive index to illustrate the microstructural change in ancient silk though the secondary structure. The disappearance of crystal planes (002) and (300) in FM and BM revealed the initial degradation occurred in amorphous region which resulted in the increase of crystallinity. The crystallinity values obtained by following eq. 1 can be used not only as an indicator to explain the fragility of aged silk, but also as a quantitive data to account for the ageing degree. Generally, oxidative degradation is the cause of ageing of polymer materials. The breakage of peptide chain may be one of the reasons why ancient silk is decayed and fragile. Thus, XPS is selected for assessing the ageing degree of ancient silk through the variation of O and C functional groups and the breakage of peptide bonds in the main chain or side chain. The gradual increase of the O/C atomic ratio disclosed different degrees of oxidative degradation happened in FM and BM with the reduction of non-oxidized carbon content. While the different N/C values C-N/C-O and C=O bond contents represent the severity of breakage of peptide bonds in the main chain or the lack of N-containing functional groups in the side chain of the ancient silk fibers. It is proved that carbon radicals participate in the deterioration process of silk where the degree of degradation is concomitant with the accumulation of carbon radicals [4]. Hence, the concentration of carbon radicals is deemed to be a reliable index in measuring the ageing of silk. And the calculated DC values intuitively describe the distinct ageing degree of ancient silk. On the other hand, analysis of amino acid is confirmed to be an incontrovertible and reliable approach in evaluating the deterioration of silk. According to the previous study [5], the amino acid compositions of silk are mainly derived by employing amino acid analyser which is a destructive method requires high consumption of sample and intricate sample pretreatment. However, the amino acids of silk can also be quantified by ¹³C CPMAS NMR analysis which is a non-destructive method with the fully recoverable of tested sample. Amongst various amino acid compositions, changes in the contents of serine and tyrosine are believed to be the valuable indicators that reflect the ageing degree of silk. ¹³C CPMAS NMR analysis can further acquire the characteristics of protein secondary structure. And the relative contents of protein secondary structure demonstrated the level of deterioration, at the same time, proved the initial degradation in the amorphous region of silk.

5. Conclusion

Silk is one of the precious artifacts that consist of crystalline region and amorphous region. Owing to its unique structure, silk is susceptible to various environmental factors which resulted in deterioration. Over the years, the degradation behaviors of silk were widely studied. However, there is a lack of systematic research on measuring and quantifying the degradation degree of ancient silk with effective ageing indicators to interpret the deterioration status. In this paper, the fresh silk and two historical silk textiles from different regions with increasing burial time were investigated by means of XRD, XPS, EPR and ¹³C CPMAS NMR. The results proved the crystallinity, oxidation and carbonization degree, variation of amino acid content and content of random coil as effective and reliable ageing indexes for explaining the ageing degree of ancient silk. This research could provide with inspirations in assessing the ageing status of silk and further provide with accurate quantitive data in comparing the degradation degree of ancient silk textiles.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

Yuxuan Gong: Investigation, Methodology, Supervision, Writing – original draft, Writing – review & editing. Zheng Li: Data curation, Formal analysis. Jianan Hu: Formal analysis, Validation. Guangzhao Zhou: Formal analysis. Guixia Xu: Formal analysis. Wenmin Yang: Formal analysis. Jinxin Zhang: Writing – review & editing.

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