Estimation of Viscoelastic Properties of Historically Important Silk Strings via NMR Spin-Lattice Relaxation Time with the Aid of Fluctuation-Dissipation Theorem

Riichiro CHUJO[1], Masako SAITO[2], Aya NAKAMURA[2], and Jun YATABE[3]

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●Keywords：Silk Strings (絹繊維), Aged Samples (劣化試料), Spin-Lattice Relaxation Time (スピン格子緩和時間), Dispersion Temperature (分散温度), tan δ (正接損失), Fluctuation-Dissipation Theorem (揺動散逸定理)

1. Introduction

Scientific approaches are growing with high rate for archaeological and historical substances. Enormous results are compiled in a monograph of Lambert (Lambert 1997). They are, however, mainly limited for dating and the identification of the substances; they are in static stage. The next stage should be in dynamic. Natural question will arise whether mechanical properties of the samples of ancient ages are different from those of the modern ages, when static characterization was performed for the former samples. The answer to the question will be obtained after the measurement of mechanical properties of the samples; the dynamic study will be required to answer. Possible candidate of dynamic study will be the estimation of mechanical properties of aged polymeric materials. The aim of the present paper is the development of the estimation method of aged polymer materials. The study will be carried out the viscoelastic properties of silk strings made in ancient ages; they are widely spread from 9th to 18th centuries. According to the classification in the Japanese history, they correspond to from Heian to Edo eras. All the silk strings in this article are come from armors and helmets. Two properties are required for armors and helmets; they are rigidity for the protection from the attack of enemy and flexibility for the smooth movement of bodies in warfield. These two properties are contradictory with each other. In order to overcome the contradiction a lot of metal pieces (for rigidity) have been linked by silk strings (for flexibility). One example is shown in Photo 1 which is the view of Tachibana Muneshige Gusoku (Sample No. 12 in Table 1).

Due to the usage of dyed silk strings armors and

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[1] Professor Emeritus, Teikyo University of Science and Technology, 15-5 Tsukushino 3-chome, Machida-shi, Tokyo 194-0001, Japan

[2] Kyoritsu Women's University, 2-1 Hitotsubashi 2-chome, Chiyoda-ku, Tokyo 101-8437, Japan

[3] Teikyo University of Science and Technology, 2525 Yatsusawa, Uenohara-shi, Yamanashi 409-0193, Japan

Photo 1 Tachibana Muneshige Gusoku

helmets have been appreciated as arts. For these strings standard viscoelastic measurements are inapplicable due to stress centralization into degraded areas; when we will try to observe the mechanical properties of aged samples via standard methods obtained results reflect those in degraded parts. In order to overcome this situation the fluctuation-dissipation theorem will serve for us. This theorem was established by Einstein (Einstein 1905) in his *annus mirabilis* (miracle year, 1905) and completed by Kubo (Kubo 1957). The application to polymeric system was developed by Okano (Okano 1963). This theorem is concerned with the equivalence between active and passive measurements. The active and passive measurements mean those perturbing molecular motion and those observing the fluctuation of molecular motion without any perturbation to the motion, respectively.

The measurements of Nuclear Magnetic Resonance (hereafter, the acronym, NMR is used) relaxation times are the representative of passive ones; in the measurements magnetic field and *rf* field are applied as perturbation to spin system not but to molecular motion.

Our strategy is as follows:

1. Spin-lattice relaxation times are observed for aged silk strings as well as fresh silk strings.
2. Mechanical properties are observed for fresh ones; they are elastic, viscous, and viscoelastic.
3. Correlation is checked between the procedures 1 and 2 for fresh samples.
4. Reduction formulae are derived the quantities obtained by the procedures 1 and 2 with good correlation.
5. Mechanical properties are estimated for aged samples with the aid of the reduction formulae obtained in the procedure 4.

This strategy is newly introduced one in order to overcome the inapplicability of standard viscoelastic measurements for aged (*i.e.*, degraded) samples.

Spin-lattice relaxation time is the measure of the relaxation in nuclear spin systems modulated by molecular motion of the lattice (which corresponds to that of molecules constituting the silk in this study). It is, therefore, the different item from viscoelastic relaxation time. Both times are closely correlated each other. The spin-lattice relaxation time is sensitive the molecular motion with 10^9 to 10^{11} Hz.

2. Experimental

2.1 Samples

All aged samples used in this article are silk strings from Japanese armors and helmets. All of them are kindly supplied by Mr. Fumio Nishioka. They have been made between 9th to 18th centuries. Details of them are compiled in Table 1. The strings used in these armors and helmets have been confirmed to be authentic.

Fresh samples were prepared in the laboratory of one (MS) of the authors. Details are compiled in Table 2.

In order to check the effect of paramagnetism of mordant to spin-lattice relaxation two kinds of mordant were used; they are $FeSO_4$ and. $KAl(SO_4)_2 \cdot$

Table 1 Details of armours and helmets used in this article

No.	Name	Era of production	Amount of *Al* /mg/1g	Amount of *Fe* /mg/1g	T_1 /sec
1	Hajinioiodoshi Yoroi	End of Heian	>3.4	<4.2	1.13
2	Akaitoodoshi Yoroi	End of Heian			0.42
3	Akaitoodoshi Yoroi	Early Kamakura	>3.4	<4.2	0.35
4	Akaitoodoshi Yoroi	Middle of Kamakura	>3.4	<4.2	0.84
5	Murasakisusogo Yoroi	Late Kamakura	2.5	4.76	1.48
6	Murasakisusogo Yoroi	Late Kamakura	<2.0	4.97	1.08
7	Akaitoodoshi Yoroi	End of Kamakura	>3.4	5.6	0.92
8	Iroiroodoshi Haramaki	Middle of Muromachi	>3.4	5.5	1.33
9	Iroiroodoshi Haramaki	Late Muromachi	n.d.	4.2	0.96
10	Murasakiitoodoshi Haramaki	Late Muromachi	>3.4	4.59	0.61
11	Kikko Kumihimo	Late Muromachi			0.80
12	Tachibana Muneshige Gusoku	Azuchi-Momoyama			0.95
13	Iroiroodoshi Nimaido Gusoku	Momoyama	<2.0	>4.2	1.55
14	Gommaido Gusoku	Early Edo			0.86
15	Namazuo-Nari Kabuto	Early Edo			0.89
16	Iroiroodoshi Haramaki	Middle or late Edo	<2.0	>4.2	0.65
17	Kurokawaodoshi Katamurasaki Domaru	Late Edo			1.84
18	Iroiroodoshi Haramaki	Late Edo			0.85

Table 2 Details of the fresh silks used in this article

No.	Species	T_1 /sec	Dispersion Temperature /°C	$\tan\delta$
21	Onichijira	0.76	222	0.133
22	Sakurahime	0.88	223	0.129
23	Matamukashi	0.65	225	0.123
24	Aojuku	0.65	220	0.142
25	Choyo	1.51	219	0.159
26	Shisensanmin	1.22	221	0.142
27	Shokei	0.74	224	0.136
28	Kankoshakken	0.59	220	0.156
29	Torukokoken	0.95	224	0.127
30	Ikoken	1.06	222	0.143
31	Hybrid. Onichijira × Naka515	1.61	213	0.176

Table 3 Details of the silks checked for the effect of mordant

No.	Fabric	Mordant	Dyestuff	Amount of *Fe* or *Al* *Fe* /mg/1.0g
41	Shungetsu × Hosho	none	none	
42	same	$FeSO_4 \cdot 7H_2O$	none	3.53
43	same	$K(AlSO_4)_2$	none	1.83
44	same	$FeSO_4 \cdot 7H_2O$	hematoxylin	4.23
45	same	$K(AlSO_4)_2$	hematoxylin	2.47

$12H_2O$. The former is paramagnetic, while the latter is diamagnetic. In this experiment hematoxylin was used as a dyestuff (not the model compound of hemoglobin). For this experiment Shungetsu × Hosho was used as silk strings.

The samples used for this purpose are compiled in Table 3.

2.2 Apparatus

^{13}C Solid-state high-resolution NMR relaxation times were measured with JEOL JNM-A500 spectrometer. Spin-lattice relaxation time was measured with conventional 180°-τ-90° pulse sequences at ambient temperature.

Viscoelasticity measurements were done with itk DVA-200s. Temperature dependence was measured in the range between ambient temperature and 300 ℃.

2.3 Experimental

2.3.1 Spin-lattice relaxation time of silk strings used in Japanese armors and helmets

As an example of ^{13}C solid-state high-resolution NMR spectra of silk strings, that of the sample 1 (Hajinioiodoshi Yoroi) is shown in Figure 1. The peak at 20.57ppm is the least coalesced with other peaks. This peak has been assigned to C_β of alanine residue. Spin-lattice elaxation time of this peak was, therefore, used as the index of "fluctuation". After the measurement of 180°-τ-90° for several τ values the logarithm of the residual magnetization (difference between equilibrium magnetization and magnetization recovery) of C_β peak was plotted against τ. This plot was automatically done by the spectrometer. The plot for the sample 1 is shown in Figure 2. Linearity of semilogarithmic magnetization recovery is still poor. However, there is no definite deviation from linearity; *i.e.*, concave or convex. If the former, Gaussian analysis should be necessary,

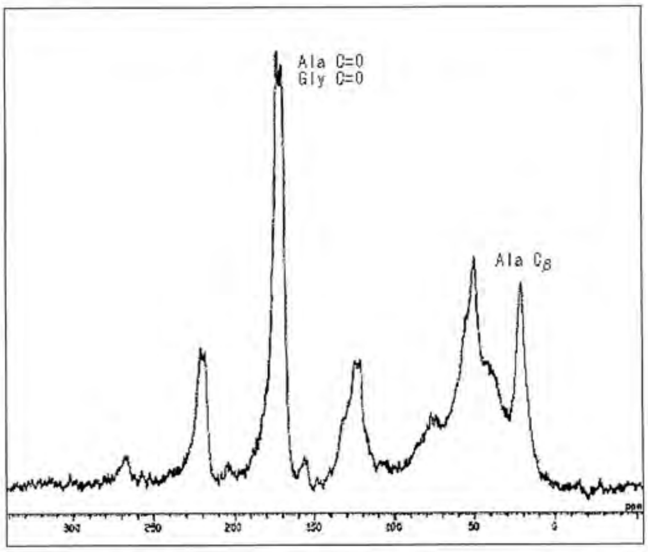

Fig. 1 ^{13}C Solid-state high-resolution NMR spectrum of the sample 1 (Hajinioiodoshi Yoroi).

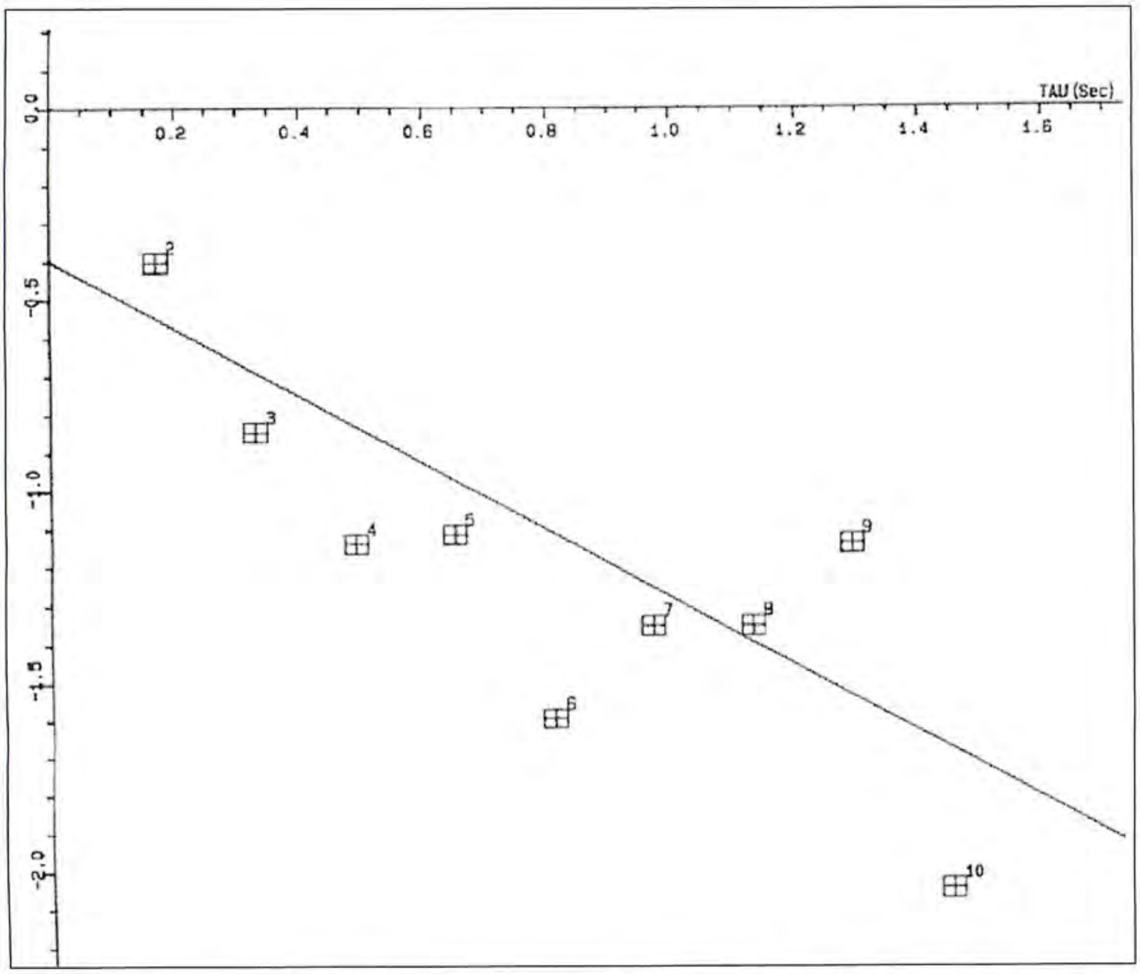

Fig. 2 Semilogarithmic plot of the residual magnetization of C_β peak after 180-τ-90° against τ for the sample 1 (Hajinioiodoshi Yoroi).

while if the latter, multi-component analysis should be required. Due to the absence of the definite deviation we did not try any of these two analyses. The straight line in the Figure 2 was also automatically drawn with the aid of least-square method by the spectrometer. Spin-lattice relaxation time was obtained from the reciprocal slope of the straight line in the figure. Obtained values were tabulated in Table 1 and Table 2.

2. 3. 2 Viscoelasticity of silk strings used in the previous paragraph

In each measurement two sheets of Kapton tape (Permacel p211 110901 GN) were prepared separated by 2 cm. After ten strings were arranged uniformly on the adhesive side (upside) they were fixed by other tapes. Temperature dispersion was measured for the prepared samples under the condition of temperature from ambient temperature to 300℃, rate of 10℃ • min^{-1}, frequency of 10 Hz, and strain up to 0.05%. After twicely repeating, averaged values were used in the following analysis.

2. 3. 3 Viscoelasticity and spin-lattice relaxation of fresh silk strings from the viscoelasticity measurements

Several quantities were obtained as the candidates of "dissipation". They are Young's modulus, ultimate strength, ultimate weight, viscosity coefficient, primary dispersion temperature, and tanδ at the temperature. The former three quantities are related to the elasticity of samples, the fourth to the viscosity, and the latter two to the viscoelasticity. Among these six quantities, for the latter two good correlation was found with spin-lattice relaxation times (For former four the results of correlation are not shown here). All samples are almost elastic; nevertheless we tried to find the correlation with NMR parameters, because there is no dissipation of energy in elasticity. Good correlation was, however, not found. Situation is similar for viscosity parameter; this is the counterpart in the storage-dissipation of energy. On the other hand, for viscoelasticity parameters better correlation was found with NMR parameters. This is the reason why the results of viscoelasticity parameters were tabulated in Table 2. These results are quite natural, because energy is dissipated in the viscoelasticity.

This kind of the difference of molecular motion can be correlated to the difference of amino acid composition (Chujo *et al.* 1996) (Data are not shown here). Silk strings are composed of fibroin which is a kind of proteins. Proteins are produced according to DNA coding. If this is the case, some apology has to be required to the difference of amino acid composition of sample by sample. In silkworm, fibroin is produced from 60-70% of amino acid fed in its wholly life (Komatsu 1994).

As a result, amino acid of composition may be modified depending on the difference of the feed. The amino acid sequence is strictly uniform in the crystalline region of fibroin. It means the sequence of amorphous region may change depending on the feed (Mita *et al.* 1994). This statement has been supported by the study of DNA sequence corresponding to fibroin (Becker *et al.* 1994).

2. 3. 4 Correlation between dispersion and fluctuation obtained from the measurements for fresh silk strings

Correlation was tried to derive between T_1 and primary dispersion temperature, and T_1 and tanδ for all 11 samples in Table 2. Correlation was considerably poor; correlation coefficients were $r^2=0.516$ and 0.433, respectively. There are two samples in whose semilogarithmic plot between the residual magnetization at τ and τ-value linearity is poor; they are samples 24 and 28 (Reason is still unclear). It means the T_1 values of the samples 24 and 28 seem to be less reliable. After removing the values of these two samples we tried to obtain the correlation between primary dispersion temperature and T_1 as well as that between tanδ and T_1. The correlations were improved much better as seen from Figure 3 and Figure 4. Reduction formulae were obtained for T_1 and primary dispersion temperature (Tmax)

$$T\text{max} = -9.86T_1 + 232, \quad r^2 = 0.822 \qquad (1)$$

and for T_1 and tanδ

$$\tan\delta = -0.0046T_1 + 0.093, \quad r^2 = 0.846 \qquad (2)$$

respectively. These two equations will be applied to estimate Tmax and tanδ for the aged samples tabulated in Table 1.

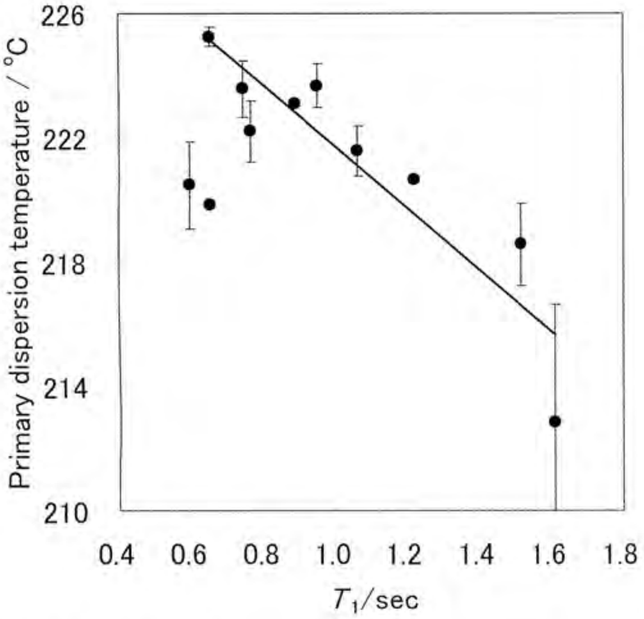

Fig. 3 Correlation between primary dispersion temperature and T_1 for fresh silk samples compiled in Table 2.

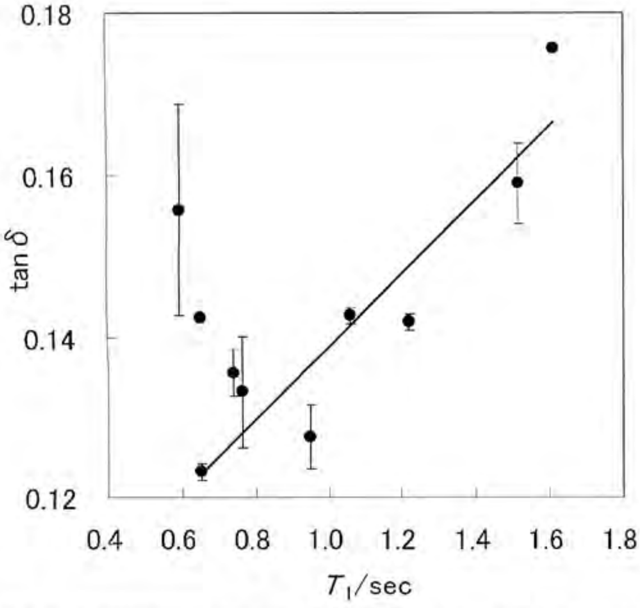

Fig. 4 Correlation between tanδ and T_1 for fresh silk samples compiled in Table 2.

2. 3. 5 Effect of ageing and paramagnetic ingredients to spin-lattice relaxation time

Before the application, we have to confirm the effect of two factors. One is the equality or similarity between NMR relaxation times of aged samples and those of corresponding fresh samples. It means whether the degradation by ageing is induced only in minor part of the samples. Only when the degradation will be induced in minor part the estimated values reflect those of corresponding fresh samples. This confirmation was already done by one (RC) of the authors with the comparison of NMR relaxation times of fresh sample and corresponding sample degraded by ^{60}Co irradiation (Chujo *et al.* 2003). In this article we refer the results of the reference instead of any further confirmation. The other confirmation is the negligibility of the effect of paramagnetic ingredients. The aged samples have been dyed by dyestuff. The mordant used in dyeing process may be paramagnetic or diamagnetic depending on the included cation. Spin-lattice relaxation is induced by paramagnetic interaction as well as dipole-dipole interaction when paramagnetic ingredients are included in the system. Only dipole-dipole interaction modulated by molecular motion is able to reflect the fluctuation corresponding to the motion. We, therefore, have to check the contribution from paramagnetic ingredients. There are mordant and blood (hemoglobin) in aged samples. The former may be included in dyeing process, while the latter may be absorbed during wearing. Observed results of T_1 were tabulated for the samples compiled in Table 4.

We can conclude that the effect of mordant is not so serious from the comparison of the numerical values of T_1 in Table 3. We are ignore the absorbed amount of blood, but supposed to be smaller than that of mordant. We can, therefore, conclude that the

Table 4 T_1 values for the samples compiled in Table 3

Sample	T_1 /sec
41	0.60
42	0.62
43	0.61
44	0.59
45	0.62

Table 5 Estimated values on viscoelasticity of the samples listed in Table 1

No.	Estimated dispersion temperature/°C	Estimated $\tan\delta$
1	220	0.145
2	227	0.112
3	228	0.109
4	223	0.132
5	217	0.161
6	221	0.143
7	222	0.135
8	218	0.154
9	222	0.137
10	226	0.121
11	224	0.130
12	222	0.136
13	216	0.164
14	223	0.132
15	223	0.134
16	225	0.123
17	213	0.177
18	223	0.132

effect of paramagnetic ingredient is negligibly small.

2.3.6 Estimation of viscoelasticity of the aged silk strings with the aid of the reduction formulae

In this paragraph two parameters on viscoelasticity of aged silk strings were estimated from the values of spin-relaxation time with the aid of the reduction formulae, Eq. (1) and (2). Results were compiled in Table 5 for the samples in Table 1. Roughly speaking, dispersion temperature and $\tan\delta$ of ancient ages silk are rather close to those of modern silk. More precisely, scattering of these values becomes smaller with going from older to closer ages. With the progress of communication and transportation system these physical properties become closer irrespective of the difference of manufactures.

3. Conclusion

Primary dispersion temperature and $\tan\delta$ were estimated for aged silk strings from NMR spin-lattice relaxation time of alanine C_β carbon with the aid of fluctuation-dissipation theorem. Those values are rather close to those of fresh silk strings. This method was applied to the comparison of these quantities between cocoons and corresponding silk strings. There was no correlation. This is due to the difference between before and after degumming.

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揺動散逸定理を使っての歴史的に重要な絹織維の粘弾性の NMR スピン格子緩和時間からの推定

中條　利一郎1)・齊藤　昌子2)・中村　亜矢2)・谷田部　純3)
1) 帝京科学大学名誉教授　〒194-0001 東京都町田市つくし野 3-15-5
2) 共立女子大学家政学部　〒101-8437 東京都千代田区一ツ橋 2-2-1
3) 帝京科学大学生命環境学部　〒409-0193 山梨県上野原市八ツ沢 2525

古い時代の試料があると，その物性を知りたくなる。しかし，絹などの繊維材料では，通常の粘弾性測定を行おうとしても，応力集中のため，不可能である。つまり，それは劣化部位の物性であって，オリジナル試料が出来た当時とは異なる。アインシュタインの揺動散逸定理によれば，揺動と散逸は同等である。通常の粘弾性測定で得られる量は散逸であり，系に力学的な摂動を加えない測定で得られるのが揺動である。NMR スピン格子緩和時間は揺動の典型である。この研究では，絹の物性を知るために，新しい試料の物性と NMR スピン格子緩和時間（T_1）を測定し，揺動散逸定理の援けを借りて両者の換算公式を求める。物性として主分散温度を用いた場合は

$$T\mathrm{max}=-9.86T_1+232$$

tanδ を用いた場合は

$$\tan\delta=0.046T_1+0.093$$

が得られる。T_1 の値の代表としてアラニン残基の C_β のそれを用いている。これらの換算公式と日本の甲冑で使われている絹織維の T_1 を測定し，上記の換算公式を用いて絹織維の粘弾性を推定する。その結果，古い時代の絹織維の物性が現代のもののそれとかなり近いことが明らかになった。