

Study on the Stress Relaxation-Time Spectrum of Pig Shoe Upper Leather

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Abstract

The stress relaxation modulus of upper leather from pigskin was investigated in this paper, and Maxwell models composed of 1-8 Maxwell units were used to try to simulate the stress relaxation behaviors of the samples. The results show that Maxwell model with 5 or more Maxwell units can simulate and describe the stress relaxation behaviors of upper leather from pigskin successfully. So the stress relaxation behaviours of the leather samples is similar to the Maxwell model with 5 Maxwell units. By the use of the stress relaxation equations obtained from model simulation and the Schwarzl relaxation-time spectrum second-order approximation method, the approximate solutions of relaxation-time spectrum may be obtained, and the stress-relaxation spectrum can be drawn. Besides, the shape of stress-relaxation spectrum was studied by means of Maxwell model and Schwarzl second order approximation method, and the accuracy degree of stress-relaxation spectrum was checked afterwards. After the verification, it is found that the accuracy of stress-relaxation spectrum was enhanced, which proves that our stress-relaxation spectrum can accurately be used to describe the stress-relaxation behavior of upper leather from pig skin.

Key words: upper leather from pigskin; stress relaxation; Maxwell model; stress relaxation-time spectrum

1. Introduction

Leather is a material derived from the biopolymer, collagen. It is widely accepted that collagen molecules consists of three polypeptide chains, each coiled in a left-handed helix. The three chains are thrown into a right-handed triple super helix stabilized by periodic hydrogen bonds. The triple helices, known also as tropocollagen, are associated laterally and longitudinally to form microfibrils. These, in turn, form fibrils aggregates of which finally aggregate to form the fiber bundles. The collagen fibrils and fiber bundles are interwoven in a three-dimensional manner through the skin. Due to the structural hierarchy of collagen and the fiber weave pattern within a hide, the leather exhibits complicated viscoelastic behaviors(Attenburrow, G. E. 1993; Manich, A M. 2006).

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In making leather, a raw, putrescible animal skin is converted into a dry, non-putrescible material with the handle and degree of flexibility required for its specific use. Several processes are important in transforming skin into leather, such as tanning, retanning, fatliquoring, finishing, etc. In order to avoid putrefaction, collagen is usually industrially modified by tanning. The essence of leather tanning is to introduce more strong and stable cross-links between collagen molecules so that the hydrothermal and mechanical stability of collagen fibers can be improved. Chrome tanning complexes, the most widely used tanning agent, can form additional cross links between collagen fibers.

Studying on the stress relaxation behavior is one of the most important ways to understand the viscoelastic properties of materials. In all the mathematical descriptions of stress relaxation, relaxation-time spectrum is widely accepted (Attenburrow, G. E. 1993; Manich, A. M. 2006). If the stress relaxation-time spectrum of a material is known, the stress relaxation behaviors the material may be successfully described. For linear viscoelastic materials, many other rheology functions such as retardation spectrum, storage modulus and loss modulus, can also be calculated with relaxation-time spectrum (Manich, A. M. et al. 2006). Therefore, it is of great significance to calculate the relaxation-time spectrum in order to well describe a material's viscoelastic properties.

The simplest mechanical model analogous to a viscoelastic system is one spring combined with one dashpot, either in series or in parallel (Manich, A. M. et al. 2006). Maxwell model, a series of a spring and a dashpot, can successfully describe the stress relaxation behavior of polymers which have only one relaxation time (Manich, A. M. et al. 2006). Most polymers, however, have a series of relaxation times due to the multiplicity of its structural units and the complexity of the molecules movement. These relaxation times can be a consecutive spectrum. Therefore, a model consists of a group of parallel Maxwell units is needed to build in order to satisfactorily imitate the stress relaxation behavior of a material (Manich, A. M. et al. 2006; Aklonis, J. J. et al. 1972).

$$E(t) = E e^{-\frac{t}{\tau}} \quad (1)$$

$$E(t) = \sum_i^n E_i e^{-t/\tau_i} \quad (2)$$

Equation (1) is mathematical expression of single Maxwell unit. Equation (2) is the expression of the model comprising a group of paralleled Maxwell units, where $E(t)$ is defined as stress relaxation modulus, n is the number of Maxwell units, E_i is defined as the spring modulus of the i th Maxwell unit and τ_i is defined as relaxation time of the i th Maxwell unit. If the number of Maxwell units increase without limit ($n \rightarrow \infty$), equation (2) can be (Manich, A. M. et al. 2006; Ferry, J. D. 1980; Aklonis, J. J. et al. 1972)

$$E(t) = \int_0^\infty f(\tau) e^{-t/\tau} d\tau \quad (3)$$

Where $f(\tau)$ is defined as relaxation-time spectrum. Actually, experience has shown that a logarithmic time scale is far more convenient, accordingly a new relaxation-time spectrum

$H(\tau)$ is defined as (Manich, A. M. et al. 2006; Ferry, J. D. 1980; Aklonis, J. J. et al. 1972)

$$H(\tau) = \tau f(\tau) \quad (4)$$

Then, equation (3) becomes

$$E(t) = \int_{-\infty}^{+\infty} H(\tau) e^{-t/\tau} d \ln \tau \quad (5)$$

Several methods are recommended in literatures to calculate $H(\tau)$. In most cases, $H(\tau)$ is calculated from dynamic viscoelastic data such as storage modulus and loss modulus (Manich, A. M. et al. 2006; Ferry, J. D. 1980; Aklonis, J. J. et al. 1972). Although equation (5) provides a way to calculate $H(\tau)$ from $E(t)$, many mathematical difficulties may be met in the calculation. To simplify the calculation, approximation methods are often used to calculate the $H(\tau)$ from $E(t)$. Equation (6) is a second-order approximation method provided by Schwarzl and Staverman

$$H(\tau) = -dE(t)/d \ln t + d^2 E(t)/d(\ln t)^2 |_{t=2\tau} \quad (6)$$

Many works have been done in the study of the stress relaxation behavior of leathers (Attenburrow, G. E. 1993; Manich, A. M. et al. 2006; Manich, A. M. et al. 2006). Komanowsky (Schwarzl, F. et al. 1953) successfully described the stress relaxation properties of leather using a six-element model consisted of three paralleled Maxwell units. He found that the relaxation modulus and relaxation times decrease with increase in fatliquor content as well as with increase in temperature and moisture content. Keyong Tang (Komanowsky, M. et al. 1995) successfully described the stress-relaxation behavior of Nappa upper pig leather using four paralleled Maxwell units. The relationship between stress-relaxation behaviors and structure of leather was also discussed in his researches.

The purpose of this paper is trying to calculate the relaxation-time spectrum of pig shoe leather using the data from the stress relaxation experiments. The calculation is based on equations (2) and equation (6).

2. Materials and methods

2.1 Materials and apparatus

The material in this experimental is finished pig shoe leather, which was kindly provided by Henan Institute of Leather & Plastic, China. Sampling positions are shown in fig.1. The dumbbell shaped samples (110mm in length and 25mm in width) were cut parallel to the backbone. The thickness of the samples was measured. Sampling machine, CPJ-25, was made by Chengde Testing Machine Factory, China. Electromechanical material testing machine, CMT6104, was made by Shenzhen Sans Testing Machine Co., Ltd, China.

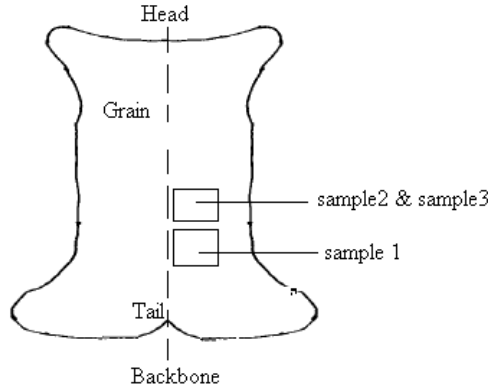


Fig.1 Sampling of the pieces used in the study

2.2 Stress-relaxation test

The leather samples were conditioned at 23 degree centigrade and the relative humidity of 50%. Before the test of stress-relaxation, several samples were stretched to get the maximum stress of the samples. The maximum stress of the samples is about 17MPa. Sample 1 was stretched at the speed of 500mm/min. When stress reached 14.2MPa, the machine was stopped to let the sample relax with the strain unchanged. The whole time of stress relaxation was 30000 seconds and the variation of stress was recorded during the process. Sample 2 and 3 were stretched to 12MPa and 6MPa, respectively, with the speed of 500mm/min, then the machine was stopped to let the samples relax. The whole time of stress relaxation was 15000 seconds.

2.3 Data process

The experimental data were processed by equation (2) with software Originpro7.5(Manich, A. M. et al. 2006)when being fitted with Maxwell models. The relaxation-time spectrums $H(\tau)$ were calculated by equation (6). The degree of approximation of $H(\tau)$ was tested by equation (5) with software Mathcad2001i(Manich, A. M. et al. 2006).

3. Results and discussion

3.1 Experimental data of stress relaxation and curves fitted by generalized Maxwell models

Fig.2 shows the data of stress relaxation of sample 1 and the curves fitted by formula of models composed by one to eight parallel Maxwell units, respectively. The squares represent experimental data and solid lines represent curves fitted by Maxwell models. The determination coefficients of the curves, fitted by different numbers of Maxwell units are shown in Table1. It can be found, from Fig.2 and Table.1, that the accuracy of the fitted curves increased markedly with the increase of the number of units from 1 to 4. The determination coefficient reaches 99.98% when the number of Maxwell units increases to 5. When the Maxwell units increased to 6, 7 and 8, the determination coefficients are same to 5 units. It demonstrates that the model composed by 5 paralleled Maxwell units can satisfactorily describe the behavior of stress relaxation of the sample 1. Table2~5 shows

rheological constants of models composed by 5,6,7,8 Maxwell units, respectively, where E_i is the spring modulus of the i th unit and τ_i is relaxation time of the i th unit. When $t=0$, the contribution of the i th unit to the whole stress is E_i , then it begins to decay exponentially with increase of t ; when $t=\tau_i$, the stress of the i th Maxwell unit decays to $1/e$ of E_i ; when $t \gg \tau_i$, the stress of the i th unit decays to 0, thus no contribution from the i th unit to the whole stress.

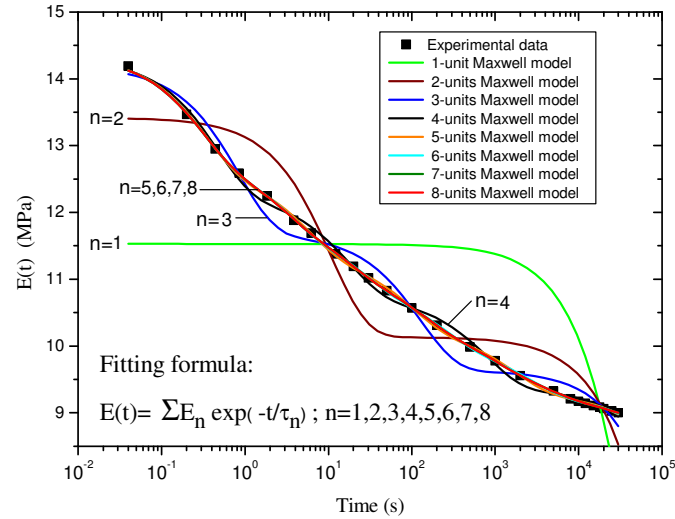


Fig.2 Experimental data of stress relaxation modulus of sample 1 and curves fitted by Maxwell models

Table 1. Determination coefficients (R^2) of curve fitting with models composed by different number of paralleled Maxwell units (sample 1)

Number of units	1	2	3	4	5	6	7	8
R^2	0.45651	0.92210	0.98732	0.99816	0.99975	0.99995	0.99998	0.99998

Table 2. Rheological constants of the model composed by 5 Maxwell units (sample 1)

E_1 (MPa)	τ_1 (s)	E_2 (MPa)	τ_2 (s)	E_3 (MPa)	τ_3 (s)	E_4 (MPa)	τ_4 (s)	E_5 (MPa)	τ_5 (s)
1.668	0.329	1.268	5.461	1.117	95.91	0.960	1712	9.276	915183

Table 3. Rheological constants of the model composed by 6 Maxwell units (sample 1)

E_1 (MPa)	τ_1 (s)	E_2 (MPa)	τ_2 (s)	E_3 (MPa)	τ_3 (s)	E_4 (MPa)	τ_4 (s)	E_5 (MPa)	τ_5 (s)
1.491	0.284	1.004	2.803	0.884	22.52	0.893	222.15	0.785	2547
E_6 (MPa)	τ_6 (s)								
9.237	1104368								

Table 4. Rheological constants of the model composed by 7 Maxwell units (sample 1)

E_1	τ_1	E_2	τ_2	E_3	τ_3	E_4	τ_4	E_5	τ_5
(MPa)	(s)	(MPa)	(s)	(MPa)	(s)	(MPa)	(s)	(MPa)	(s)
1.429	0.272	0.893	2.172	0.845	14.14	0.801	115.04	0.591	764.16
E_6	τ_6	E_7	τ_7						
(MPa)	(s)	(MPa)	(s)						
0.551	4124	9.187	1450297						

Table 5. Rheological constants of the model composed by 8 Maxwell units (sample 1)

E_1	τ_1	E_2	τ_2	E_3	τ_3	E_4	τ_4	E_5	τ_5
(MPa)	(s)	(MPa)	(s)	(MPa)	(s)	(MPa)	(s)	(MPa)	(s)
1.429	0.272	0.892	2.167	0.844	14.08	0.796	113.86	0.575	734.09
E_6	τ_6	E_7	τ_7	E_8	τ_8				
(MPa)	(s)	(MPa)	(s)	(MPa)	(s)				
0.539	3751	0.522	58167	8.699	22661630				

3.2 The second-order approximation expression of stress relaxation-time spectrum

The second-order approximation of stress relaxation-time spectrum can be calculated from stress relaxation modulus $E(t)$ with equation (2) and (6) when expression of $E(t)$ has the form of equation (2). By differentiating equation (2) with respect to the $\ln(t)$ in the first and second order, we obtain

$$\frac{d(E_i e^{\frac{-t}{\tau_i}})}{d(\ln t)} = -\frac{E_i}{\tau_i} e^{\frac{-t}{\tau_i}} \quad (7)$$

$$\frac{d^2(E_i e^{\frac{-t}{\tau_i}})}{d(\ln t)^2} = -\frac{E_i}{\tau_i} e^{\frac{-t}{\tau_i}} + \frac{E_i}{\tau_i^2} e^{\frac{-t}{\tau_i}} t^2 \quad (8)$$

When equation (7) and (8) were applied in equation (6), equation (9) was obtained.

$$H(\tau) = \sum_{i=1}^n \frac{E_i}{\tau_i} e^{\frac{-\tau}{\tau_i}} - \sum_{i=1}^n \frac{E_i}{\tau_i} e^{\frac{-\tau}{\tau_i}} + \sum_{i=1}^n \frac{E_i}{\tau_i^2} e^{\frac{-\tau}{\tau_i}} \tau^2 \Big|_{t=2\tau} \quad (9)$$

When equation (9) was simplified, equation (10) was obtained.

$$H(\tau) = \sum_{i=1}^n \frac{4E_i}{\tau_i^2} \cdot \tau^2 \cdot e^{-2\tau/\tau_i} \quad (10)$$

Equation (10) is the equation of stress relaxation modulus ($E(t)$) expressed in the second-order approximation stress relaxation-time spectrum ($H(\tau)$) of generalized Maxwell models. The E_i and τ_i is the elastic modulus and stress relaxation time of the i th Maxwell unit, respectively. Equation (10) provides an easy way to calculate the relaxation-time spectrum. If the stress relaxation behaviors of a material can be described by Maxwell model successfully, the

second-order approximate relaxation-time spectrum may be obtained when the stress relaxation modulus E_i and stress relaxation time τ_i are applied in equation (10).

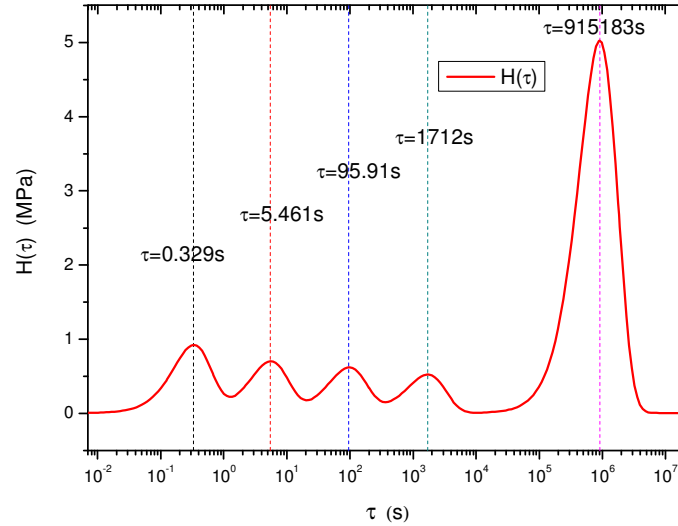


Fig.3 Stress relaxation-time spectrum of sample 1

Since the model consist of 5 Maxwell units can well describe the stress relaxation behavior of sample 1, it is reasonable to calculate the stress relaxation-time spectrum of sample 1 by the data obtained by such a model. When all the value of E_i and τ_i shown in Table2 are applied to equation (10), the stress relaxation-time spectrum ($H(\tau)$) of sample 1 can be obtained. The Fig.3 shows the stress relaxation-time spectrum. From this figure, it can be found that $H(\tau)$ has 5 peaks. The horizontal coordinate of every summit is approximately equal to the relaxation time of every Maxwell unit if we contrast data of the Table 2, the ratio of vertical ordinate of every summit to spring modulus of every unit is approximately equal and the ratio of half peak width to relaxation time of every unit is also equal in a rough.

In order to understand the relation between $H(\tau)$ and rheologic constants of every Maxwell unit more clearly, each section of equation (10) was plotted respectively and fig.4 was obtained. Fig.4 shows that the plot of every section has only one peak, the contribution of each section to the whole stress relaxation-time spectrum ($H(\tau)$) reaches to the maximum (peak height) when $\tau = \tau_i$ and decays to 0 when $\tau < \tau_i$ or $\tau > \tau_i$. The peak height, the corresponding horizontal coordinate and half peak width were calculated by equation (10) and shown in Table 6, where E_i and τ_i are the stress relaxation modulus and relaxation time of the i th Maxwell unit respectively. Table 6 also shows that, the i th peak height is directly proportional to E_i and the ratio of peak height to E_i is $4/e^2$; the horizon ordinate of the crest of the i th peak is equal to τ_i ; the half peak breadth of the i th peak is directly proportional to τ_i .

Table 6. Rheological constants of sections of each stress relaxation-time spectrum (sample 1)

Section of $H(\tau)$	1	2	3	4	5
E_i (MPa)	1.668	1.268	1.117	0.960	9.276
τ_i (s)	0.329	5.461	95.91	1712	915183
Peak height (MPa)	0.903	0.687	0.605	0.520	5.022
Abscissa of crest (s)	0.329	5.461	95.91	1712	915183
Half peak width (s)	0.558	9.270	162.8	2906	1553395
Peak height/ E_i	0.541	0.542	0.542	0.542	0.541
Half peak width/ τ_i	1.696	1.697	1.697	1.697	1.697

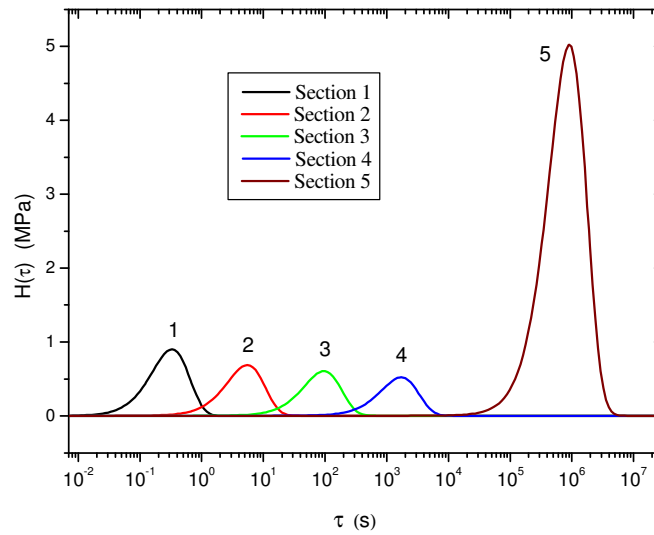


Fig.4 Sections of stress relaxation-time spectrum of sample 1

3.3 Approximation degree of stress relaxation-time spectrum

To test the approximation degree of stress relaxation-time spectrum obtained, $H(\tau)$ is used to calculate the stress relaxation modulus $E(t)$ and the results are used to compare with those experimental data. When equation (10), which expresses the stress relaxation-time spectrum, is applied to equation (5), equation (11) was obtained.

$$E(t) = \sum_{i=1}^n \frac{4E_i}{\tau_i^2} \int_{-\infty}^{+\infty} \tau^2 \cdot e^{-2\tau/\tau_i} \cdot e^{-t/\tau} d \ln \tau \quad (11)$$

Change the integration variable of equation (11), we obtain

$$E(t) = \sum_{i=1}^n \frac{4E_i}{\tau_i^2} \int_0^{\infty} \tau \cdot e^{-2\tau/\tau_i} \cdot e^{-t/\tau} d \tau \quad (12)$$

Where both E_i and τ_i have the same meaning with those in equation (2), represent the modulus and relaxation time of the i th Maxwell unit respectively. If the values of E_i and τ_i are known, $E(t)$ can be calculated by equation (12). When the data of E_i and τ_i in the Table 2~5 are

applied in equation (12), the $E(t)$ of sample 1 calculated by $H(\tau)$ that consist of 5, 6, 7 and 8 Maxwell units respectively can be obtained as shown in table 7.

Table 7 shows that, for the models consisted of 5, 6, 7 and 8 Maxwell units, the $E(t)$ calculated by $H(\tau)$ are very close to the experimental data for sample 1. The difference among the $E(t)$ calculated by models consisted of different numbers of Maxwell units were neglected.

Table 7. Experimental and calculation of $E(t)$ by $H(\tau)$ (sample 1)

Time (s)	Measurement $E(t)$ (MPa)	Calculation $E(t)$ n=5 (MPa)	Error n=5 (MPa)	Calculation $E(t)$ n=6 (MPa)	Error n=6 (MPa)	Calculation $E(t)$ n=7 (MPa)	Error n=7 (MPa)	Calculation $E(t)$ n=8 (MPa)	Error n=8 (MPa)
0.00	14.295	14.335	-0.040	14.389	-0.094	14.296	-0.001	14.296	-0.001
0.20	13.467	13.333	0.134	13.374	0.093	13.279	0.188	13.279	0.188
0.44	12.950	12.876	0.074	12.927	0.023	12.835	0.115	12.835	0.115
0.85	12.588	12.520	0.068	12.576	0.012	12.483	0.105	12.483	0.105
1.85	12.243	12.161	0.082	12.208	0.035	12.113	0.130	12.113	0.130
3.85	11.881	11.837	0.044	11.877	0.004	11.783	0.098	11.783	0.098
6.27	11.691	11.614	0.077	11.661	0.030	11.569	0.122	11.569	0.122
12.30	11.381	11.319	0.062	11.377	0.004	11.285	0.096	11.285	0.096
20.06	11.191	11.127	0.064	11.179	0.012	11.087	0.104	11.087	0.104
30.31	11.018	10.974	0.044	11.016	0.002	10.924	0.094	10.924	0.094
50.16	10.829	10.787	0.042	10.822	0.007	10.731	0.098	10.731	0.098
100.1	10.570	10.517	0.053	10.566	0.004	10.474	0.096	10.474	0.096
200.7	10.312	10.252	0.059	10.317	-0.005	10.221	0.091	10.221	0.091
500.1	9.984	9.957	0.027	10.033	-0.049	9.911	0.073	9.912	0.072
1001	9.777	9.749	0.028	9.698	0.079	9.698	0.079	9.698	0.079
2000	9.553	9.538	0.015	9.504	0.049	9.500	0.053	9.501	0.052
5001	9.325	9.295	0.030	9.268	0.057	9.272	0.053	9.276	0.049
8001	9.209	9.192	0.017	9.159	0.050	9.169	0.040	9.179	0.030
10008	9.171	9.128	0.043	9.076	0.095	9.064	0.107	9.088	0.083
12099	9.144	9.089	0.055	9.044	0.100	9.039	0.105	9.067	0.077
15033	9.106	9.035	0.071	8.999	0.107	9.005	0.101	9.041	0.065
18002	9.083	8.982	0.101	8.955	0.128	8.970	0.113	9.016	0.067
20000	9.063	8.947	0.116	8.925	0.138	8.947	0.116	9.001	0.062
25000	9.027	8.860	0.167	8.852	0.175	8.890	0.137	8.967	0.060
30000	9.001	8.775	0.226	8.781	0.220	8.835	0.166	8.937	0.064
Average absolute error (MPa)		0.066		0.063		0.099		0.084	
Average relative error		0.7%		0.6%		1%		0.8%	

The values of $E(t)$ in calculation and experiment are shown in Fig.5. The squares represent measurement data. The solid, dot, short dash and dash lines represent the data calculated by $H(\tau)$ that with 5, 6, 7, 8 Maxwell units, respectively. The figure shows that there is a good coincidence between experimental data and the calculated data for every model and these curves nearly overlap each other.

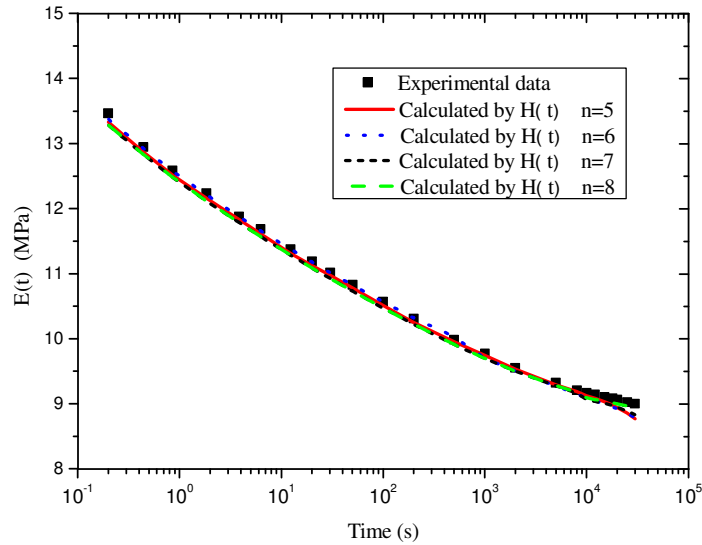


Fig.5 Experimental data and calculated data of $E(t)$ by $H(\tau)$ (sample 1)

To test the applicability of equation (10) for leather materials, the experimental data of samples 2 and 3 are simulated with generalized Maxwell models with 5 Maxwell units. The rheologic constants were applied in equation (12) to calculate the value of $E(t)$. Fig.6 is the plot of experimental data and calculated data of stress relaxation modulus. The squares and circles represent experimental data of sample 2 and 3 respectively, and the solid and dash lines represent the calculated data of sample 2 and 3 respectively. Fig.6 shows that for both samples, the calculated data are quite coincident with the experimental data. It has demonstrated that the equation (10) can well describe the stress relaxation spectrum of the pig shoe upper leather.

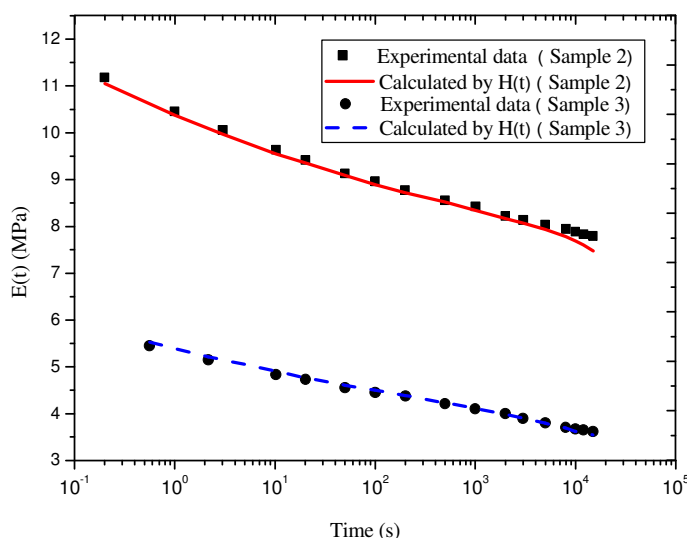


Fig.6 Experimental data and calculated data of $E(t)$ by $H(\tau)$ ($n=5$) (samples 2 & 3)

4. Conclusions

The stress relaxation behavior of pig shoe upper leather material can be successfully simulated by the generalized Maxwell models consisted of 5 or more paralleled Maxwell units. The stress relaxation-time spectrum of pig shoe upper leather material can be conveniently calculated by a second-order approximate method from Schwarzl if the rheological constants of every Maxwell unit are known. The relaxation-time spectrum calculated in this paper can well describe the stress relaxation behavior of pig shoe upper leather material.

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6. References

- Aklonis, J. J.; Macknight, W. J.; Shen, M. Introduction to Polymer Viscoelasticity. Wiley-Interscience: New York, 1972.
- Alfrey, T. Mechanical Behavior of High Polymers, Interscience: New York, 1948.
- Attenburrow, G. E. J Soc Leather Technol Chem 1993, 77, 107.
- Ferry, J. D. Viscoelastic Properties of Polymers. 3rd ed., Wiley: New York, 1980.
- Ferry, J. D.; Williams, M. L. J Colloid Sci 1952, 7, 346
- Komanowsky, M.; Cooke, P. H.; Damert, W. C. Kronick, P. L.; McClintick, M. D. J Am Leather Chem Assoc 1995, 90, 243.
- Manich, A. M.; de Castellar, M. D.; Berania Gonzalez.; Ussman, M. H.; Marsal, A. J Soc Leather Technol Chem 2006, 90, 102.
- Manich, A. M.; de Castellar, M. D.; Berania Gonzalez.; Ussman, M. H.; Marsal, A. J Appl Polym Sci 2006, 102, 6000.

Mathcad 2001i. Mathsoft Engineering & Education, Inc.
Origin Pro 7.5. Originlab Corporation.
Schwarzl, F. A.; Staverman, J. J Appl Phys 1952, 23, 838.
Schwarzl, F.A.; Staverman, A. J. Appl Sci Res 1953, A4,127
Schwarzl, F. R. Rheo Acta, 1971, 10, 165.
Tang, K.Y.; Wu, D.C. China leather, 2000, 29, 20
Ward, I. M. Mechanical Properties of Solid Polymers, 2nd Ed. Wiley-Interscience: New York, 1983.
Williams, M. L.; Ferry, J. D. J Polym Sci 1953, 11, 169.