Influence of moisture content and time on the mechanical behavior of polymer material

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Abstract The effects of moisture content and time on mechanical behavior of polymer materials are investigated both theoretically and experimentally in this paper. An equivalence relationship between time intervals and the moisture content for polymer nylon-6 has been established by way of experimental observation and measured results. The relationship shows that there exists equivalence between moisture and service time in affecting mechanical properties. In other words, an increase in moisture can be replaced by prolonging acting time in producing the same effect on material properties. Consequently, a moisture-time superposition principle is presented based on the experimental results and the analogy of temperature-time superposition principle. Numerical results such as stress-strain curves with different moisture contents are presented to verify the applicability and correctness. The proposed method appears very promising in study on the effect of moisture content on mechanical behavior of polymer materials.

Keywords: equivalence relationship of moisture-time, moisture content, mechanical properties, shift function.

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Studies on the effect of environmental factor and time on mechanical behavior of macromolecular polymers are of scientific significance and engineering importance and has attracted considerable researchers in both material science and applied mechanics. In recent years, the macromolecular polymer has got wide applications in architectural materials, micro-electronic devices, and micro-machine because they have low costs, are easy to manufacture, and possess good heat-resistant and insulation properties. Noting that polymer components are usually very small in space dimension and large in surface, their properties are easy to be affected by various environmental factors such as moisture and temperature. In addition, under long-time service macromolecular polymer will suffer from aging too. Therefore it is important to investigate the effect of various environmental factors on material properties of macromolecular polymer in achieving high performance of the materials.

Studies in the past focused on two major environmental factors: temperature and moisture. Research on the effect of temperature on macromolecule polymer can be traced back to very long ago and the corresponding theories have been well documented. These theories, especially the equivalence relationships of temperature-time, are very useful in understanding the mechanism on how the properties of macromolecule polymer can be affected by environmental temperature. In contrast, study on the effect of environmental moisture is later than that of temperature although it is now getting more and more attention of researchers in this field due to the following two main reasons. First, reliability problem due to material cracking, material expansion, and the stress concentration, may be present in polymer components when subject to improper moisture contents. Second, improper moisture contents may speed up the aging process of macromolecular polymer.

Current research effort on the effect of moisture contents on macromolecular polymer has been mainly focused on the following two distinct aspects[1]. One is on residual stress and deformation induced by moisture expansion of the materials. The analysis on this problem is quite similar to that in the analysis on the effect of temperature on material properties[2]. Following this line, Lee[3] investigated the stress singularity between film and the rigid substrate induced by both moisture and temperature. Xu et al.[4] investigated the effect of moisture on crack energy of TiN/SiO_2 in multi-film configuration. Whitney et al.[5] analyzed the moisture inflation in polymer by using the approach similar to that of temperature inflation and showed that the inflation strain and moisture inflation coefficient can be measured through experiment. Studies on structure stresses and interface stresses caused by penetration diffusion of moisture were reported in ref. [6]. Based on linear elasticity theory, Chang[7] analyzed the mechanical behavior of a pipe subjected to both moisture and temperature change; Tsai[8] reported the influence of temperature-moisture on steam pressure and structure performance; Aboudia and Williams[9] studied theoretically the diffusion of moisture and temperature and their coupling with stress fields. The second aspect deals with the influence of moisture on the mechanical behavior such as Young's modulus, density, and service life[10]. Kang and her associates[11, 12] investigated experimentally the effect of relative moisture environment on material properties of thin films. Following this line, Liu and Hwang[13] analyzed the reliability of micro-electronic structure due to environmental humidity with the numerical simulation method. They pointed out that moisture plays an important role in fiber degeneration. Gampp et al.[14] in their aging test observed that the aging process can be sped up by adjusting temperature and moisture to a certain degree.

Time experience or service time can also affect significantly the material properties of polymer structures. In the past several decades much work has been done on the equivalence of temperature and acting time. Consequently, many experimental and theoretical results have been reported. In contrast, there is very little work reported on the equivalence relationship between moisture and time. Biliaderis et al.[15] studied the effect of temperature on vitrescible temperature using the so-called temperature-time superposition principle. Schapery[16] pointed out that the accelerating factor can be used in treating viscoelastic or viscoplastic polymers when considering the effects of stress, temperature fields, moisture, and aging. Maka et al.[17] evaluated the shift factor and other material parameters by using creep curve, and then predicted the aging performance of the polymer under consideration. Kasapis[18] suggested that WLF equation can be mended by considering moisture parameter as a variable to be capable of modelling moisture problem. Mamesjet[19] presented detailed derivation of temperature-time superposition principle and indicated the possibility of the existence of equivalence between moisture and time. To our knowledge, however, there is little work available in literature on the effect of moisture contents on physical and mechanical properties of polymers. In particular, there is a lack of the experimental confirmation about the moisture-time equivalence principle for macromolecular polymers. Kang[20] has done some original work on this fields.

In this paper the effect of moisture content and time factor on material performance is investigated both theoretically and experimentally. The equivalence between moisture and time is analyzed experimentally and then, the moisture-time superposition principle is presented and derived theoretically. Numerical results, such as stress-strain curve (or modulus-strain curve) for different moisture contents, are presented to verify the applicability and correctness.

1 Experiment on the basic mechanical performance of nylon-6 at different moisture contents

In this section we will study how the mechanical behavior of polymer can be affected by moisture contents through tensile test. The nylon-6 was selected as testing samples because it has highly hygroscopic capacity and thus it is easy to perform moisture analysis. The dimension of nylon-6 used in the experiment is shown in fig. 1. The moisture here can be described by using either moisture content or relative moisture. The former means the saturation of moisture state in a sample and the latter is the difference of the moisture between the sample and the environment surrounding the sample. It is proved that the moisture content is more suitable than relative moisture for the purpose of investigating the effect of moisture-time equivalence relation on material behavior of materials. Therefore the moisture content, rather than relative moisture, is used throughout this paper.

Various moisture contents of the testing samples are acquired by dipping method and are quantified by sensitive weighing device. The moisture contents of the specimens were measured as 1.6%, 2.0%, 2.5%, 3.0%, 3.8%, 5.1%, 5.7% and 8.3%. During the measure-

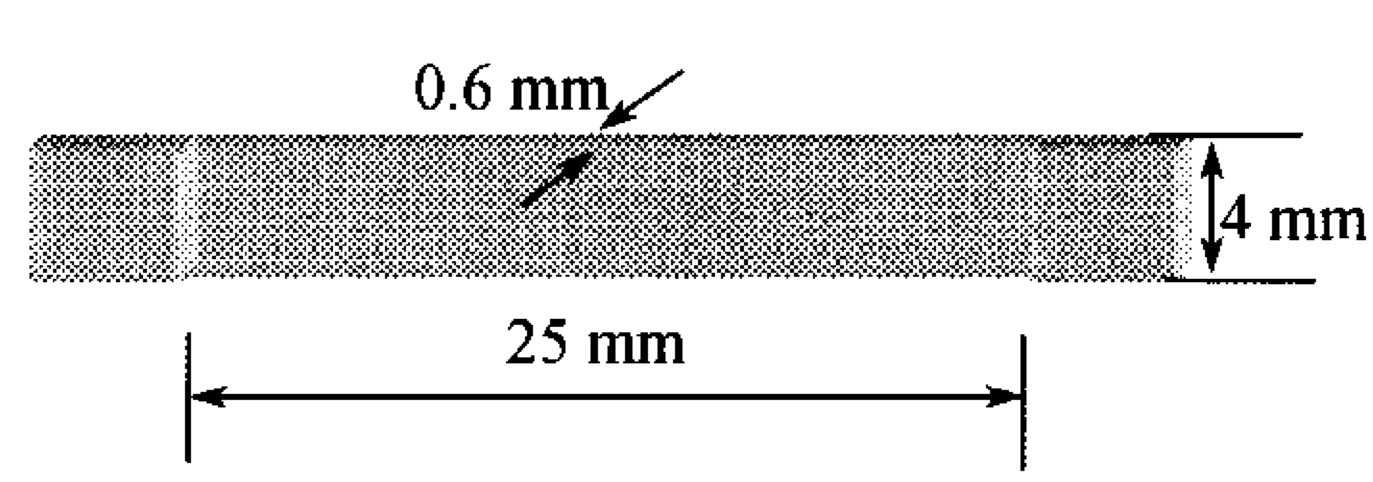

Fig. 1. The size of nylon-6 sample.

ment the ambient temperature has been kept constant at 24℃. The experiment has been carried out on a CSS-44100 electronic universal testing-machine. The crossbeam speed has been set at 0.1/min.

Fig. 2 shows the stress-strain relationship for different moisture contents. It can be seen that moisture has an obvious effect on mechanical property of the materials, and the strength of the material decreases along with the increase in moisture. Typically, the elastic modulus, elastic limit, and yield limit decrease along with an increase in moisture. In order to describe conveniently the mechanical performance of material at different stages, a variable is introduced and named instant module (module for short) which is the ratio of strain to stress. The reciprocal of module called creep compliance is also frequently used when describing the performance of the material. Based on the results in fig. 2, figs. 3 and 4 present the module-strain curve for different moisture contents and the module-moisture content curves for different strains, respectively.

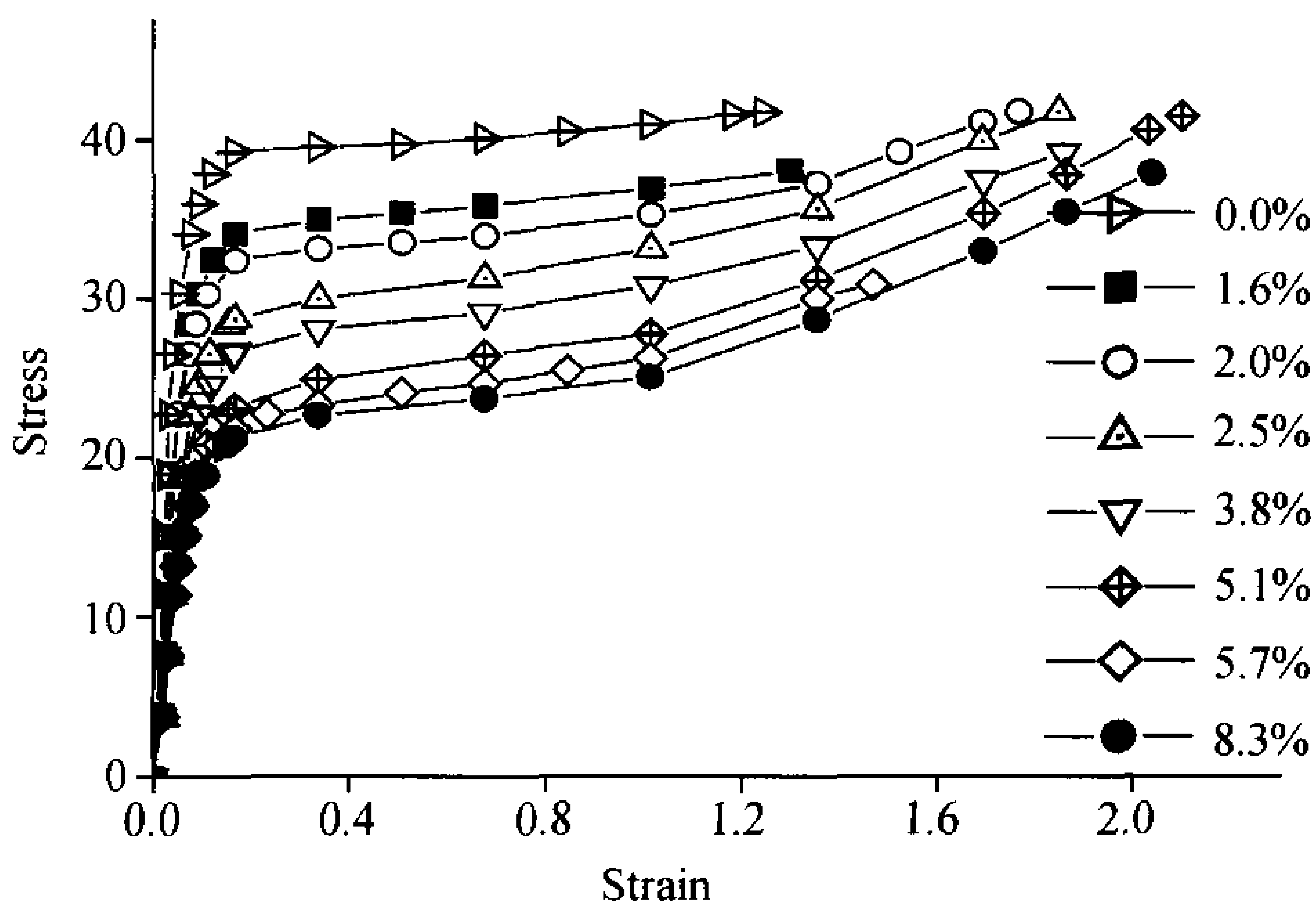

Fig. 2. Stress-strain curves of nylon-6 for different moisture contents.

It is evident from the module-strain curve in fig. 3 that the effect of moisture decreases along with the increase in strain. It can also be seen from fig. 4 that the effect of moisture content on module is obvious, especially when the moisture is less than 4%. The relation between moisture and module is approximately linear when the moisture is less than 4%. After that, the material module keeps nearly constant and seems not to be affected by moisture. In addition, it is also found from fig. 2 that the yielding of the material is affected by moisture significantly and a relationship between them can be established accordingly.

2 Stress analysis of the experiment on equivalent moisture-time relationship

2.1 Two key problems in the experiment

There are two major problems to be fixed in the experimental research on the effect of moisture and time on the mechanical performance. The first one is how to keep the moisture content constant or stable in the whole process of experiment as the moisture

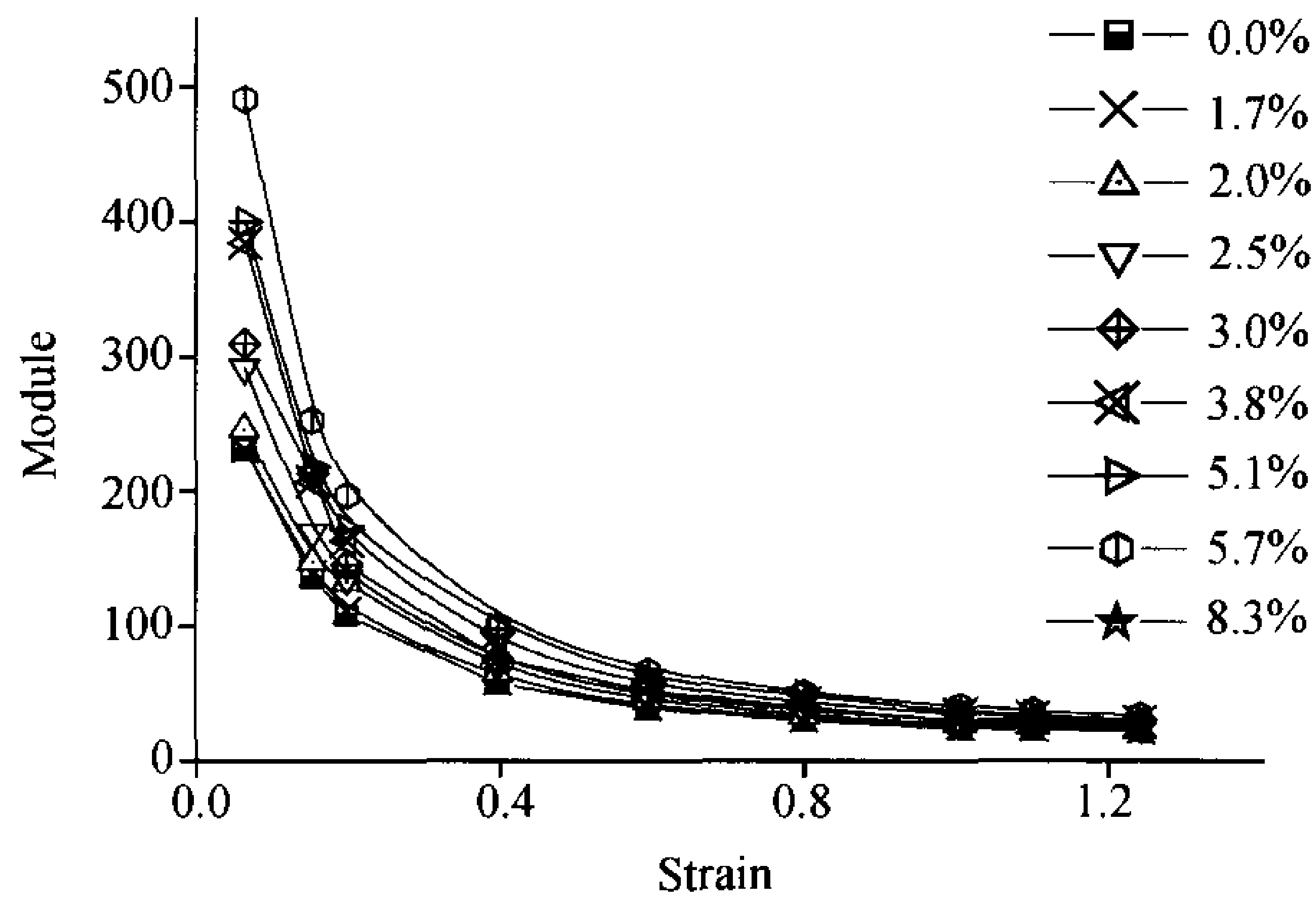

Fig. 3. Module-strain curves of nylon-6 for different moisture contents.

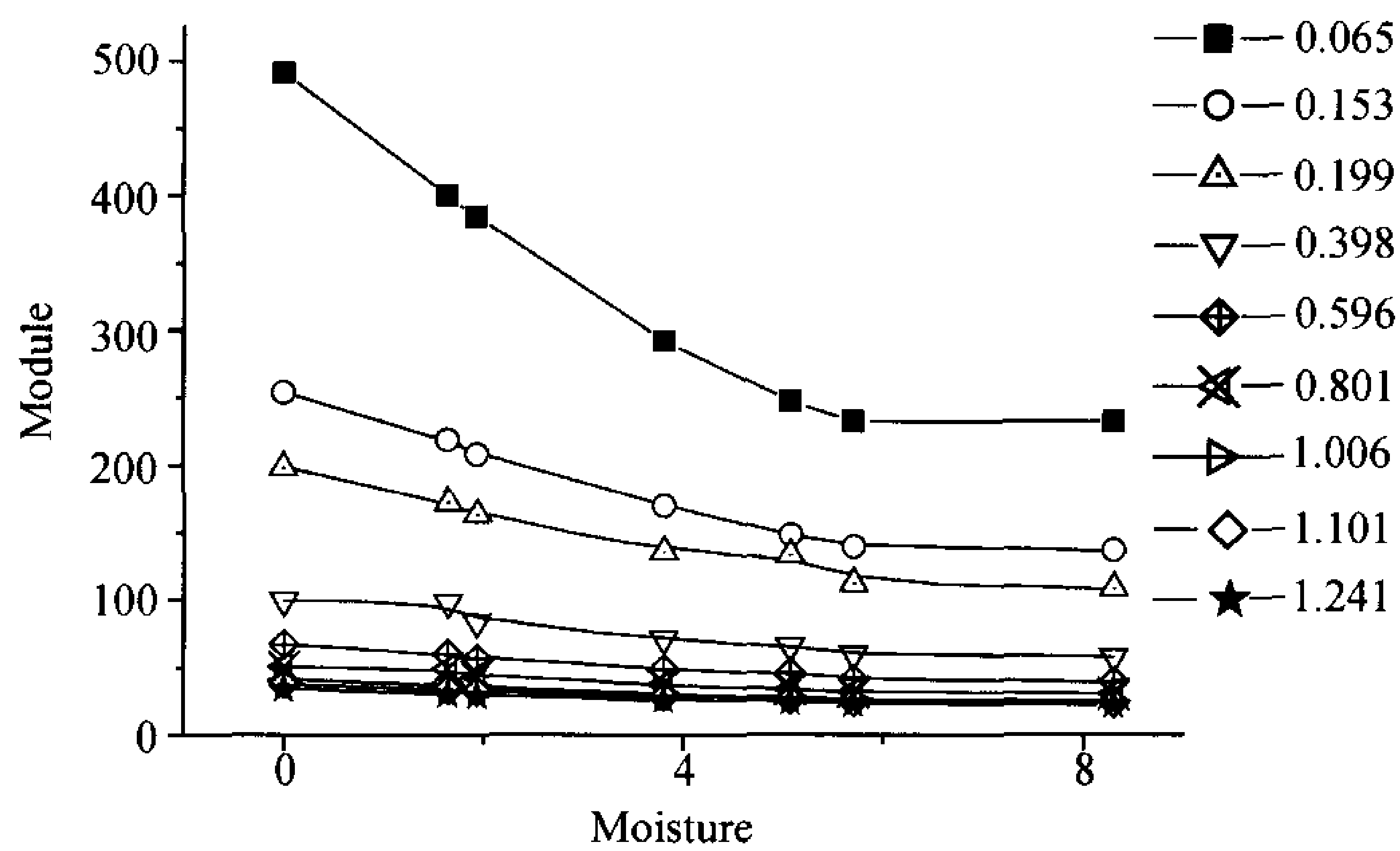

Fig. 4. Module-moisture curves of nylon-6 for different strains.

content may go away when the sample is placed in a high temperature environment. In this work a series of methods were presented to solve this problem. For example, we can keep the moisture content of the sample stable by controlling environmental moisture within a specified range. Moreover macromolecular films are usually very thin and thus may experience a wide range of deformation such as elastic, plastic or viscoplastic deformation. An efficacious optical experimental method[22] called digital marker correlation is introduced for this purpose. This method is untouchable and is suitable for measuring large deformations presented in thin and soft materials.

2.2 Experiment on moisture-time superposition

A series of experiments on moisture-time superposition have been carried out to establish the moisture-time relationship of polymer materials. In the experiment the moisture content of material was kept constant by adjusting the environment humidity within a specified range.

Fig. 5 presents the compliance as a function of time experience for different moisture contents. The curves in fig. 6 show the corresponding compliance which is the re-

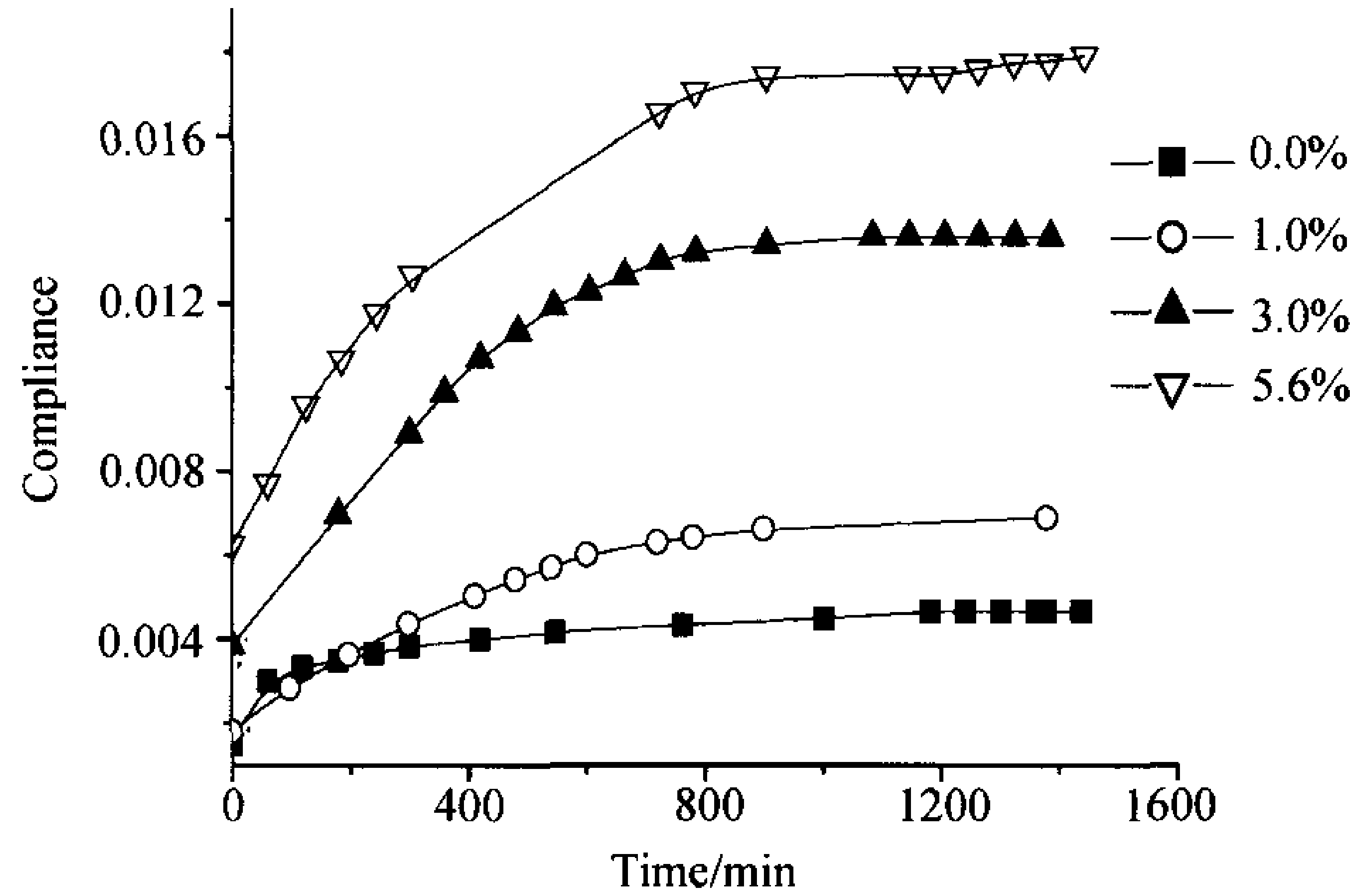

Fig. 5. Compliance-time curve of nylon-6 for different moisture contents under the lading N=40 N.

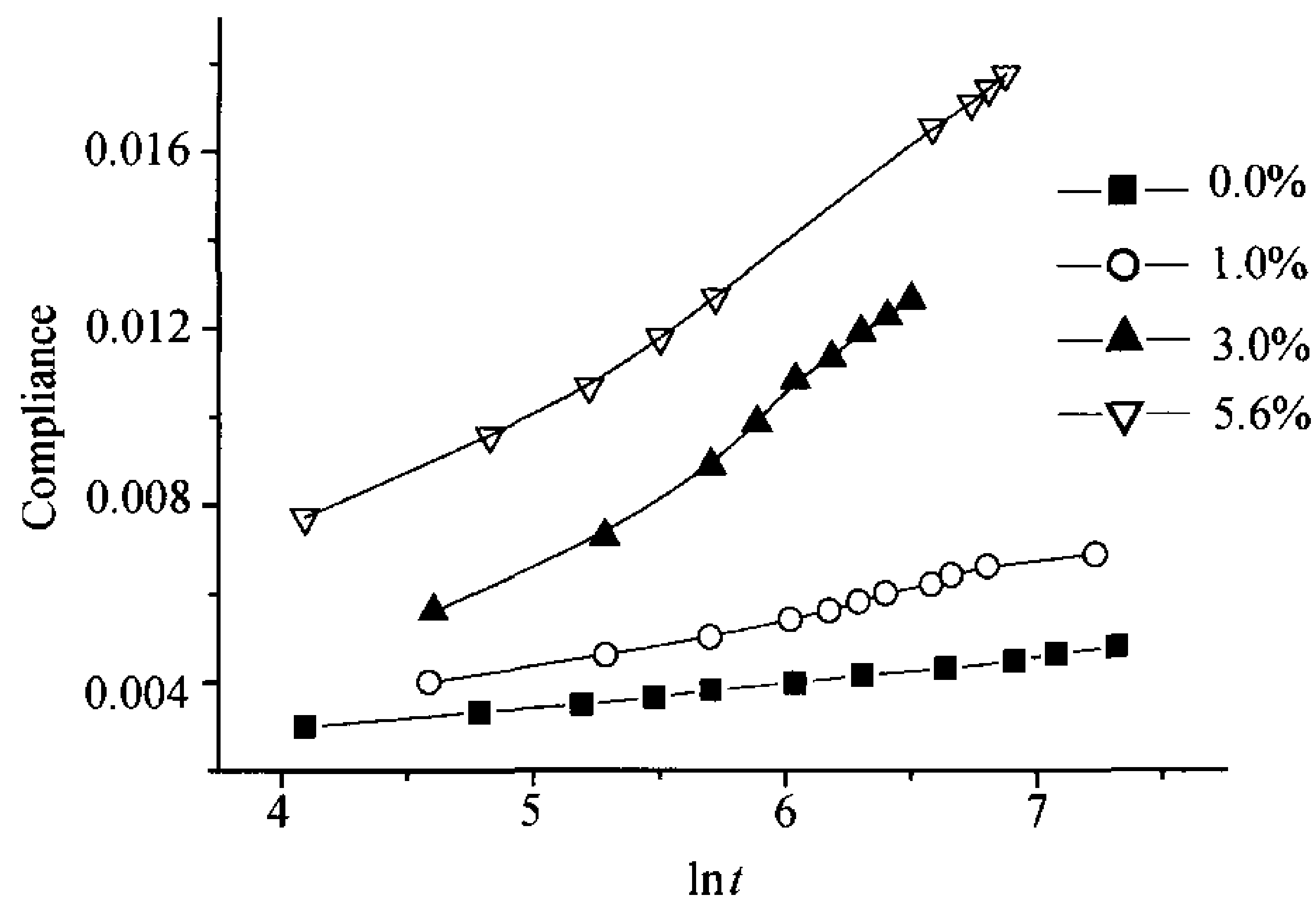

Fig. 6. Compliance-ln$t$ curve of nylon-6 for different moisture contents under the lading N=40 N.

ciprocal of module[19] versus the logarithm of time. It is found that the creep behavior is quite sensitive to the moisture contents. It should be mentioned that the curve of creep versus moisture contents discussed above can be shifted by a constant ln a_T to form a generalized curve[19] and thus some equivalence between moisture and time can be established. As was pointed out by Mamesjet[19], a generalized curve defined as a creep curve was, in fact, obtained from the original curve shifting based on the time-temperature superposition principle rather than from experimental results directly. Using this approach, fig. 7 is obtained by shifting all four curves in fig. 6 to the location of the creep curve with the moisture content 1.0% and then they are joined together. Fig. 7 actually represents the generalized curve with moisture content 1.0%. It indicates that there exists some equivalence between moisture and time for producing the same effect on mechanical property. The generalized curves for other moisture contents can be similarly obtained and are given in fig. 8. Using the generalized curves for different moisture, the equivalent material characteristics related to time can be predicted for other moisture conditions.

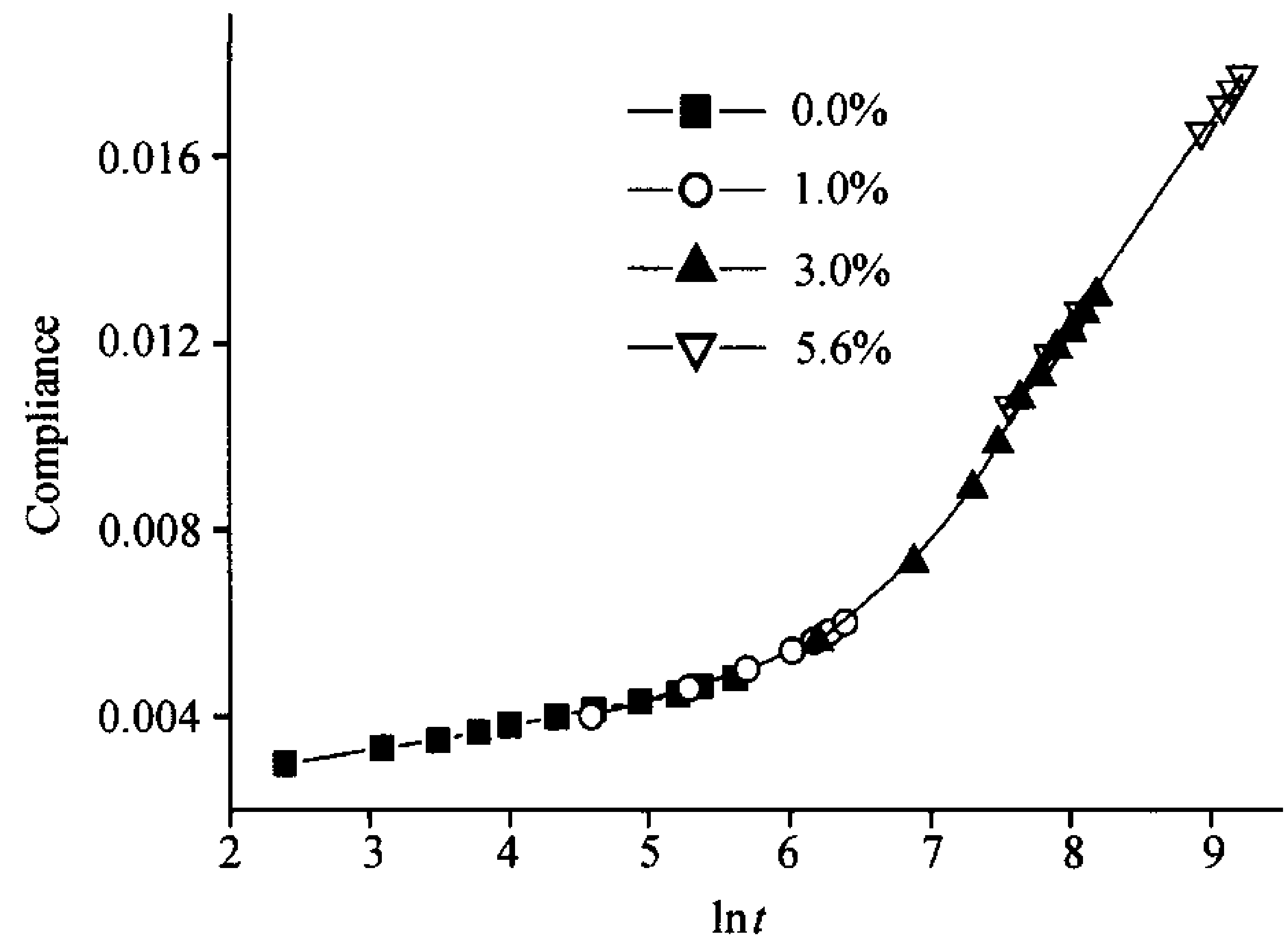

Fig. 7. Compliance-ln$t$ generalized curve by shift factor for the moisture content 1.0% in fig. 6.

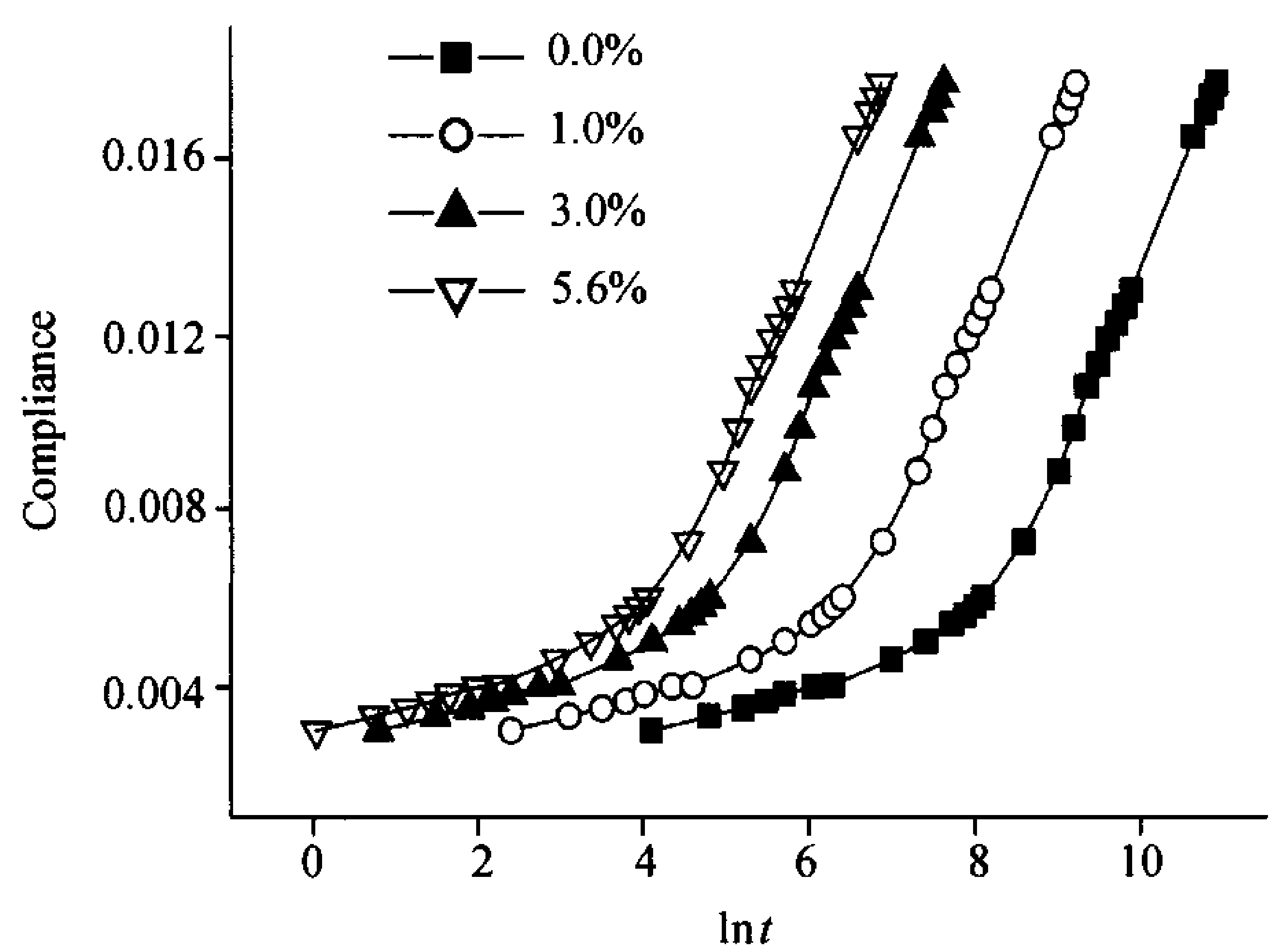

Fig. 8. Generalized curves under other moisture contents.

3 Moisture-time superposition principle

The equivalence relationship of temperature and time experience provides a theoretical support for describing constitutive equations of viscoelastic materials or predicting material properties under transient temperature field and long term loading. It is found from the experiment of moisture-time superposition discussed above that there exists some equivalence between moisture and time, analogous to the equivalence between temperature and time. In this section, the moisture-time equivalence was quantitatively analyzed and detailed derivation of the corresponding formulation was presented based on the temperature-time superposition principle[19].

3.1 Shift factor and shift function

The equivalence between moisture and time can be established based on the concept of the shift function and shift factor which are determined from the experimental results. Following the way of ref. [19], the shift factor, say logarithm a_M, can be defined as

$$\ln a_M = f(M - M_0), \tag{1}$$

where M stands for moisture content, M_0 is the referenced moisture content (M_0=1.0% in our analysis); f is a function of variable (M−M_0), which can be fitted in a way described below.

The curve of $\ln a_M$ versus time can be plotted based on the shift factor obtained from experiments. The function used to fit the curve is defined as follows:

$$y = y_0 + A_1 \times [1 - \exp(-x / t_1)] + A_2 \times [1 - \exp(-x / t_2)], \tag{2}$$

where y stands for $\ln a_M$, and y_0 , A_1, A_2, t_1 and t_2 are parameters.

The fitting results are shown in fig. 9, which presents a curve of the following shift function:

$$\ln \alpha_M = 0.17 + 2.49 \times \left[1 - \exp\left(-(M - M_0)/2.55\right)\right]. \tag{3}$$

Similarly, if referenced moisture content M_0=0 was selected, the fit curve can also be obtained and is shown in fig. 10. But the related shift function now becomes

$$\ln \alpha_M = -0.05 + 4.41 \times \left[1 - \exp\left(-(M - M_0)/2.55\right)\right]. \tag{4}$$

Based on the shift function and the generalized curve above, the generalized curve for other moisture contents can be obtained similarly and we omit those details here.

3.2 The moisture-time superposition principle

For linear viscoelastic material, the constitutive equation has the following form:

$$\sigma = \eta \frac{d\varepsilon}{dt}, \tag{5}$$

where σ stands for stress, ε is strain, and η is the coefficient of viscosity. Generally, η varies with both temperature and moisture, i.e. $\eta = \eta(T, M)$. If a constant temperature environment is considered, the coefficient of viscosity is a function of moisture only. In this case $\eta = \eta(M)$. The time scale can be changed from t to t' according to the following equation:

$$\eta(M_0)\frac{d\varepsilon}{dt'} = \eta(M)\frac{d\varepsilon}{dt}, \tag{6}$$

where t' denotes the convective time.

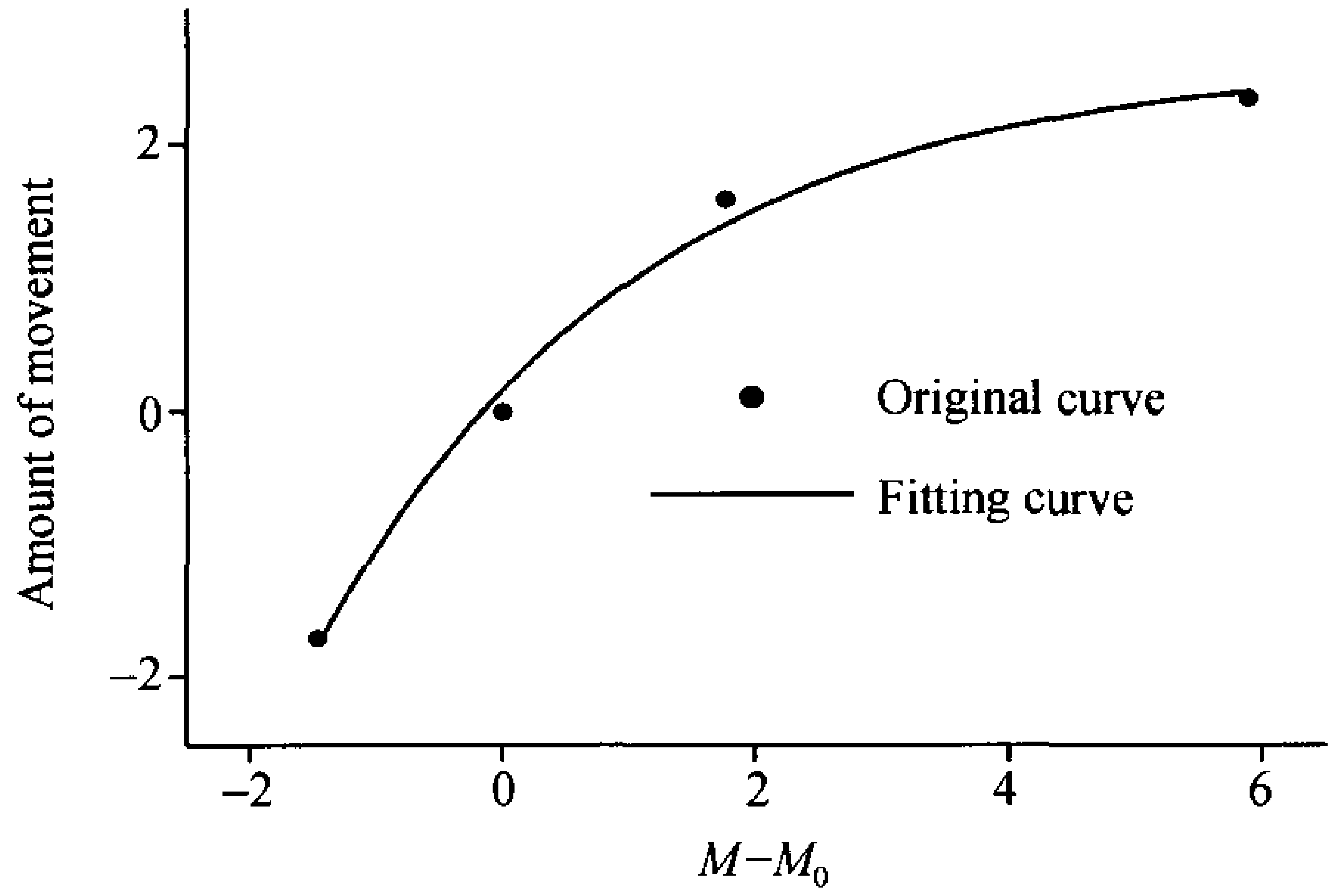

Fig. 9. $\ln a_M$-$(M-M_0)$ curve with M_0=1.0%.

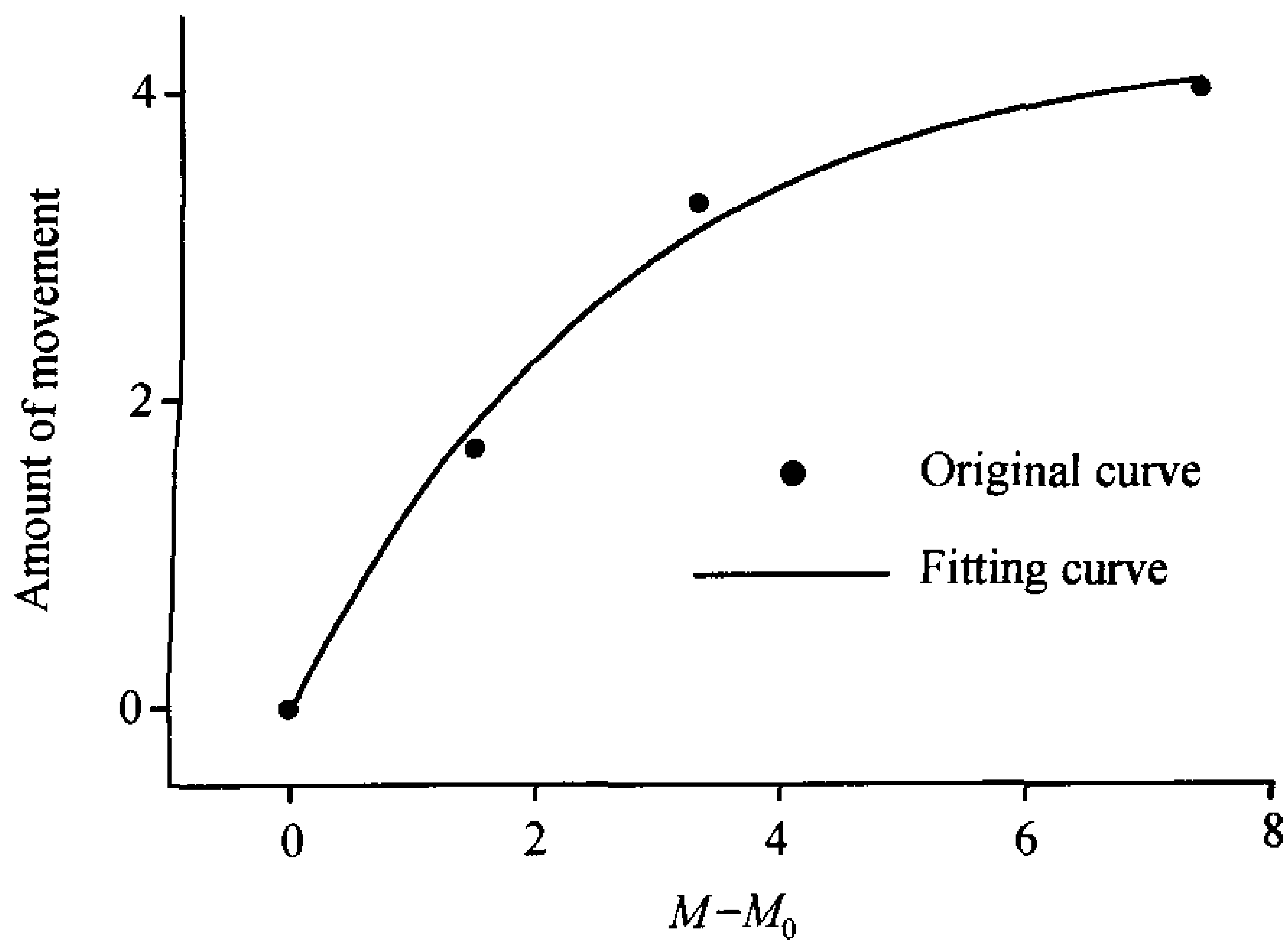

Fig. 10. $\ln a_M$-$(M-M_0)$ curve with M_0=0.

With eq. (6) the relationship between stress and strain rate subject to a moisture content M can be written in terms of the referenced moisture content M_0. The coefficient of viscosity $\eta(M)$ can thus be expressed in the form

$$\eta(M)=\frac{\eta(M_0)}{a_M(M,M_0)}, \tag{7}$$

where a_M denotes a function of moisture.

From eqs. (6) and (7) the relation between t and t' can be written as

$$dt'=a_M dt \quad \text{or} \quad t'=\int_0^t a_M dt. \tag{8}$$

For a constant moisture field, eq. (8) becomes

$$a_M = \text{const}, \quad t'=a_M t. \tag{9}$$

Considering next a typical solid whose relaxation time is $n = n_0 / a_M$, the constitutive equation in this case is written in the form[19]

$$H \frac{n_0}{a_M} \frac{d\varepsilon}{dt} + E\varepsilon = \frac{n_0}{a_M} \frac{d\sigma}{dt} + \sigma , \tag{10}$$

where H stands for the modulus of instantaneous elasticity, E the sustained modulus of elasticity, and n_0 the relaxed time factor at M_0.

Using eq. (8), eq. (10) can be rewritten as

$$H n_0 \frac{d\varepsilon}{dt'} + E\varepsilon = n_0 \frac{d\sigma}{dt'} + \sigma . \tag{11}$$

This equation models the strain process of a typical solid under variable moisture contents, while eq. (10) describes the strain process with constant moisture content only. The difference between them is due to the time variable (t for eq. (10) and t' for eq. (11)). Therefore formulations obtained from the condition of constant moisture content can also be used to model the process with variable moisture contents if we replace t with t'. This forms the basic idea of moisture-time superposition principle. In other words, if the coefficient a_M of a material in a certain time interval is known, the constitutive equation of this material can be written as[19]

$$\varepsilon(t) = \frac{\sigma(t)}{H} + \int_0^t K(t-\tau, M)\sigma(\tau)d\tau , \tag{12}$$

where K is a kernel function which is defined in ref. [20].

As discussed above and noting eq. (8), the relation between stress and strain at any moisture content can be acquired by replacing t with t' in eq. (12):

$$\varepsilon(t') = \frac{\sigma(t')}{H} + \int_0^{t'} K_0(t'-\tau')\sigma(\tau')d\tau' . \tag{13}$$

In eq. (13), $\sigma(t')$ contains the unknown function $a_M(M)$. The function can be determined from the results of creep experiment.

If $\sigma = \sigma_0$ is a constant, the strain can be expressed in terms of conversive time by using eq. (13):

$$\frac{\varepsilon}{\sigma_0} = f(t') = f = f(a_M t), \tag{14}$$

where f is again a function of time.

For a typical material with the following constitutive equation[19]:

$$\frac{\varepsilon(t)}{\sigma_0}=\frac{1}{E}+\left(\frac{1}{H}-\frac{1}{E}\right)e^{-\frac{E}{Hn_0}a_M t}, \tag{15}$$

some creep curves of $\varepsilon - t$ can be obtained from eq. (14). The major difference among these curves is due to their velocity of creep. The velocity of creep will generally increase along with an increase in moisture. If creep curves under any moisture contents can be expressed by half logarithmic coordinate system ($\ln t, \varepsilon/\sigma_0$), the function a_M can be determined accordingly. Using the relation $\ln t' = \ln t + \ln a_M$, eq. (14) can be rewritten in the form

$$\varepsilon/\sigma_0 = f(t') = f_1(\ln t') = f_1(\ln t + \ln a_M). \tag{16}$$

Eq. (16) indicates that all creep curves are parallel and the shifting amount between any two curves is $\ln a_M(M)$. In order to determine the function $\ln a_M(M)$, consider the $\varepsilon/\sigma_0 - \ln t$ curve for n different values of the moisture content M_k ($k = 1, \ldots, n$). Calculate the shifted amount between each of these curves and the curve with moisture content M_0 and denote it as $\ln a_M(M_k)$. The function $\ln a_M(M)$ can thus be determined with the interpolation method based on the n values of $\ln a_M(M)$.

The analysis above reveals that there exists equivalence between moisture and time from the viewpoint of their effects on material properties. For example, a typical amount of mechanical relaxation can be attained by putting the sample in a chamber either with higher moisture for a shorter time interval or with lower moisture but for a longer time interval. In other words increasing moisture content can be replaced by prolonging the time interval in affecting molecule motion and viscoelastic behavior of polymer. This principle is known as moisture-time superposition principle. Using the principle, the viscoelastic data, including creep, stress relaxation, and dynamic variable, which were obtained from creep experiments or stress relaxation experiments with different moisture contents, can be superposed by shifting the curve along the time axis. The shifting amount a_M is usually called shift factor. With the time-moisture superposition principle the relationship below holds true for any one material parameter E:

$$E(M, t) = E(M_0, t/a_M). \tag{17}$$

In addition, following the way of the temperature-time superposition principle[19] the shift function $\ln a_M$ can be expressed in terms of $(M - M_0)$ as follows:

$$\lg a_M = c\,(M - M_0), \tag{18}$$

where c is a material coefficient. This equation enables us to determine the shift function more easily if the parameter c is known. Alternatively, the shift function can be determined by curve fitting using the results of experiment (see section 2 for details).

4 Conclusions

The effect of moisture contents on mechanical properties of macromolecule polymer is studied systemically in this paper. The findings of this work can be summarized as follows:

i) The effect of moisture content on basic mechanical property of macromolecule polymer was investigated both experimentally and theoretically. In particular, the experimental research on moisture-time superposition principle was carried out systematically. Based on the experimental results we found first that there is an equivalence relationship between time and moisture. The shift factor and shift function of nylon-6, which appeared in the equivalence relationship, can be determined from creep experiments.

ii) Based on the experimental results theoretical analysis and derivation were carried out on the equivalence between moisture and time. Numerical results are presented to verify the effectiveness and correctness of the proposed formulation.

iii) A series of experimental approaches such as digital marker correlation method were introduced into moisture experiment with which the moisture content in a sample can be kept stable for a relatively long period and the measurement of large deformation in creep experiment can be made effectively.

The results on the equivalence between moisture and time in this paper presents a promising approach to treating problems of macromolecular polymer affected by moisture and other environmental factors. Further extension of this work is possible such as to the coupling effect of aging on material properties and moisture and moisture-temperature-time relationship in producing equivalent effect on material behaviours.

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