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Some comments on the penetration of water vapor into regenerated silk fibroin

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Abstract

The data of the penetrating behavior of water into silk fibroin and of the softening behavior of the film by penetration has been reviewed on the basis of fractal conception. Two power laws have been obtained from the logarithmic plot for the data. A convenient fractal figure has been presented in order to interpret the power laws and the penetrating and softening behavior. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Regenerated silk fibroin; Penetration of water; Fractal structure

1. Introduction

In recent years, there is a growing tendency to view silk fibroin more as a functional material rather than a textile material. For example, the possibility of it being an enzyme substrate [1,2], its permeability to oxygen gas [3,4] and its characteristics in blood compatibility [5] have been investigated in the biotechnological and biomedical fields. Such functional performances are concerned with the amorphous region and not with the crystal region of silk fibroin. Accordingly, an investigation on the morphology of the amorphous region is necessary for its development as a functional material. However, it is not easy to grasp microscopic details of the amorphous region, and a lot is unknown for active research [6–8].

In such circumstances, we have investigated the morphology of the amorphous region through measurements of penetrating behavior of water into the material. A structural model, in which the amorphous region constitutes two different aggregated structures, has been assumed on the basis of the results obtained from integral sorption experiments [9]. Successive differential sorption curves measured subsequently can be successfully explained with the structural model [10]. An approach from a different point of view has also been attempted where the mechanical properties of silk fibroin films containing water has been measured [11]. The softening behavior of the films has not been at variance with the conclusion derived from sorption experiments.

In the meantime, the usefulness of the new conception "fractal" is noted in the field of polymer science [12]. The complex behavior and critical phenomenon observed for polymers has been successfully explained by employing this conception [13]. Thus, we have tried to review the data of the penetrating behavior of water into silk fibroin and of the softening behavior of the film by penetration of water on the basis of fractal conception. This paper reports two power laws obtained from the logarithmic plot for the data, and shows a convenient fractal figure to interpret the penetrating and softening behavior.

2. Penetrating behavior

The discussion on the penetration of water vapor into the material is based on the data [10] obtained from successive differential sorption experiments [14]. Fig. 1 gives a part of the experimental data, a series of sorption curves a–j. Here the ordinate represents the mass of water in grams per gram of polymer at time *t* and the abscissa square root of time per film thickness.

The curves are divided into first and second in the way shown in the figure. This is because the first and second steps have been ascribed to the sorption of water into two different aggregated structures in the amorphous region of

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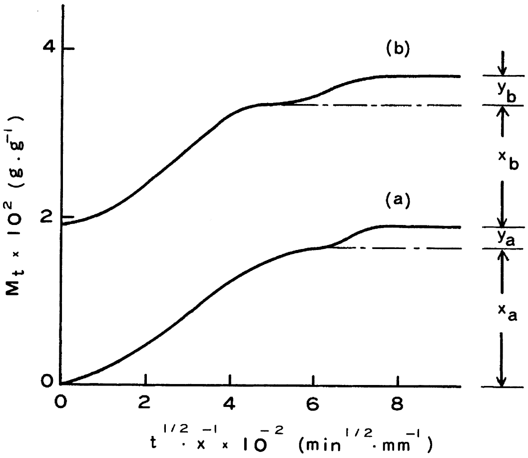

Fig. 1. Successive differential sorptions for water vapor into silk fibroin film at 30°C. Pressure intervals from initial pressure p_i mmHg to equilibrium pressure p_f mmHg: (a) 0 → 1.0; (b) 1.0 → 3.3

the material [9,10]. The aggregated structure corresponding to the first step has been termed structure 1 (S_1). S_1 is considered to be similar to the structure in common amorphous polymers [15,16], because the shape of the first step varies according to the following scheme by the penetration of water vapor: sigmoid type → two-stage type → pseudo-Fickian type → Fickian type. The second step going up to equilibrium after the first step has been ascribed to a more tightly aggregated structure distinguished from the common amorphous structure. This aggregated structure has been termed structure 2 (S_2).

x_a and y_a in the figure indicate the amount of water allotted to the first and second steps of the sorption curve a. This means that S_1 and S_2 took up just x_a and y_a of water by the change of water vapor pressures, p_i: 0 mmHg → p_f:1.0 mmHg. The differential sorption curves b–j were divided into two parts in the same way, and $x_b \sim x_j$ and $y_b \sim y_j$ were determined. The plots of the sum of x or of y against the equilibrium vapor pressure yields the sorption isotherms for S_1 or for S_2 (the isotherms are not shown in the present paper). The amounts of water sorbed in S_1 and S_2 under a certain vapor pressure can be read off from those sorption isotherms and the amounts (grams per gram of polymer) are termed M_1 and M_2, respectively.

At first the penetration of vapor into the amorphous region of polymers is caused by rearrangement of segments. S_1 and S_2 will form certain microphase structures, and so the sorption by these structures will not be independent. Thus, the plot of M_2 against M_1 is expected to exhibit the influence of sorption by S_1 on penetration of water into S_2. As can be seen from the plot shown in Fig. 2(a), M_2 increases linearly in the region of small M_1, however, the data for M_1 greater than some critical value deviates gradually from the straight line. This suggests that penetration in the region beyond the critical value is governed by another mechanism different from that giving the straight line. The point e can be regarded as a critical point in penetrating behavior. Thus, the curve has been divided into two parts as shown in the figure. The shaded part of Fig. 2(a) has been reproduced in the plot of m_2 against m_1 in Fig. 2(b). We have tried the logarithmic plot for the data in the figure in order to examine the correlation between m_1 and m_2. The plot illustrated in Fig. 3 shows that the points g ~ j follow a straight line. This means that the power law $m_2 \sim (m_1)^a$ holds good for the shaded part. It is known that the power law demonstrates correlation between two parameters and the parameters that are not correlative obey the exponential function [17,18]. Fig. 3 indicates clearly that the penetration of water into S_2 is affected by the water content in S_1.

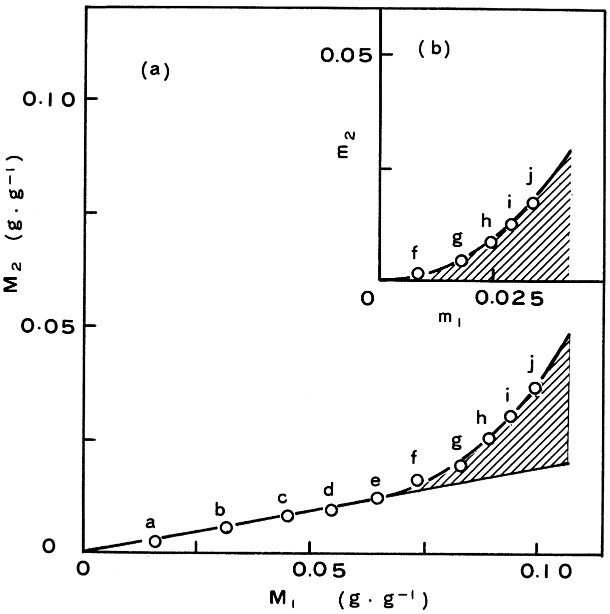

Fig. 2. (a) Plot of amounts (M_2) of water sorbed in structure 2 against amounts (M_1) sorbed in structure 1. Letters a ~ j correspond to successive differential sorptions a ~ j in Fig. 3 of Ref. [10]. (b) Reproduction of shaded part of (a).

Incidentally, the first-step of differential sorptions for points f and g is the two-stage type, and that for points h and i is of pseudo-Fickian and Fickian, respectively [10]. These shapes of sorption show that S_1 is gradually loosened around the points f and g by the penetration of water, and undergoes so-called isothermal glass–rubber transition around the points h and i [17].

After all, the penetrating behavior for the range of large M_1 is interpreted as follows. S_1 undergoes glass–rubber transition by the penetration of water. Such a morphological change accelerates the rearrangement of the segments of S_2. The steep increase of amounts of water sorbed in the material reflects such circumstances.

3. Softening behavior

The softening of material caused by penetration of water is discussed on the basis of the elongation data of films measured

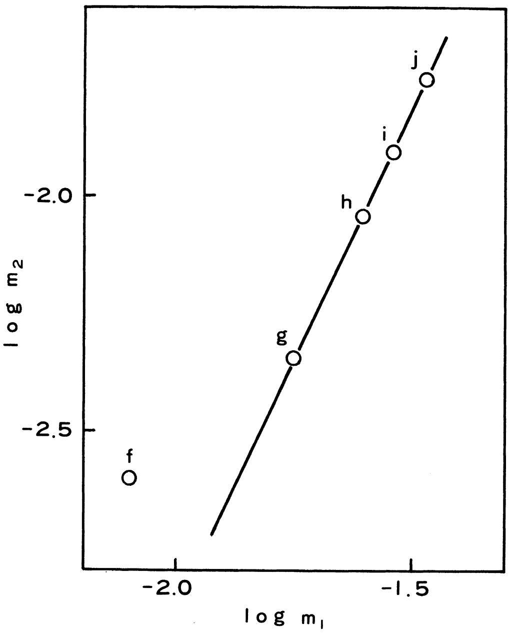

Fig. 3. Logarithmic plot for Fig. 2(b).

under controlled humidity [11]. These elongation–humidity data can be converted into the elongation against amounts of sorbed water, by employing the sorption isotherm for the silk fibroin–water vapor system [10]. Fig. 4(a) shows the relationship between degrees of elongation and amounts of water sorbed in the material. Here the ordinate represents elongation in centimeters per centimeter of film, and the abscissa mass of water in grams per gram of polymer.

It is found that the film is a bit elongated in the range of small amounts of sorbed water, and that the degrees of elongation increase gently up to about 0.09 g/g of sorbed water and then increase steeply beyond this critical point. In manner similar to the penetrating behavior, the curve has been divided into two parts. The shaded part has been reproduced and shown in Fig. 4(b). The logarithmic plot for the data of Fig. 4(b) is shown in Fig. 5. The points follow a straight line, that is, the power law $l \sim (m)^{b}$ holds good for shaded parts. This exhibits the correlation between elongation and amounts of water sorbed in the material.

Softening is a practical concept for glass–rubber transition. The value of 0.09 g/g is close to the water concentration for glass–rubber transition of S_1 [10]. The figure indicates that the penetration of just a little water is effective for softening of films beyond the critical point. The power law is the mathematical expression for the correlation between softening and penetration of water. The softening behavior can be interpreted in the same way as the penetrating behavior described above.

4. Power law and fractal structure

The power laws $m_2 \sim (m_1)^{a}$ and $l \sim (m)^{b}$ have been obtained for the penetrating and softening behavior. The relations have been interpreted in connection with the structural model derived from differential sorption experiments.

Incidentally, there are two attractive papers dealing with the glass–rubber transition of polymers. One is concerned with the approach based on percolation theory by Cohen and Grest [19]. The percolation theory has strongly suggested that the relationship S/V–s^{-k} holds good for the mixture of solid and liquid around the glass–rubber transition point [20,21], where s is the mass of liquid, S the surface area and S/V the surface-to-volume ratio of liquid clusters. They have considered that the dispersion of relaxation time τ is due to the dispersion of the S/V value and, therefore, the relationship $\tau = \tau_0 s^{-k}$ is set up. Consequently, they have derived the relaxation function of the extended exponential type $R(t) = \exp[-(t/\tau)^{z}]$. The other is the paper by Hodge and Huvard [22]. They have interpreted the anomalous behavior of heat capacity of polystyrene in the glass transition range by assuming structural relaxation of the extended exponential type. The calculated curves by employing the function $\phi(t) = \exp[-(t/\tau_0)^{\beta}]$ were in good agreement with the experimental data.

The extended exponential function is closely related to the fractal usually characterized by the power law. In

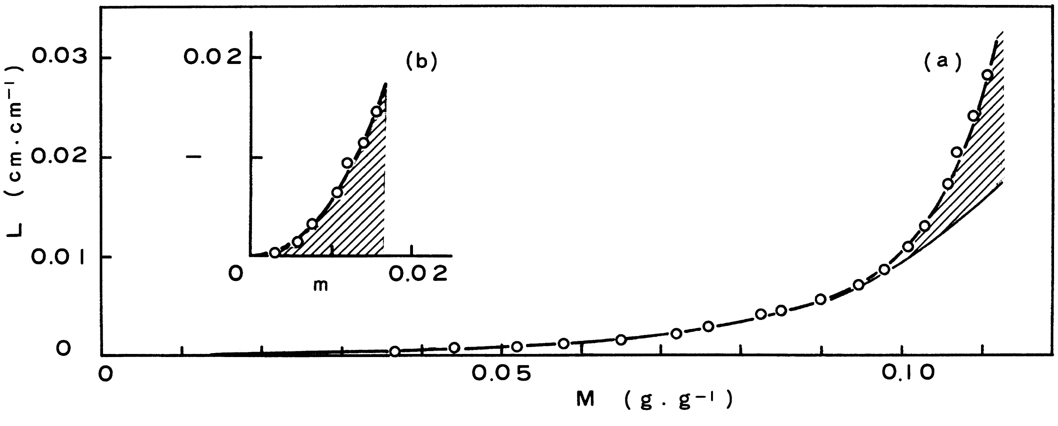

Fig. 4. (a) Plot of degrees of elongation against amounts of water sorbed in silk fibroin film. (b) Reproduction of shaded part of (a).

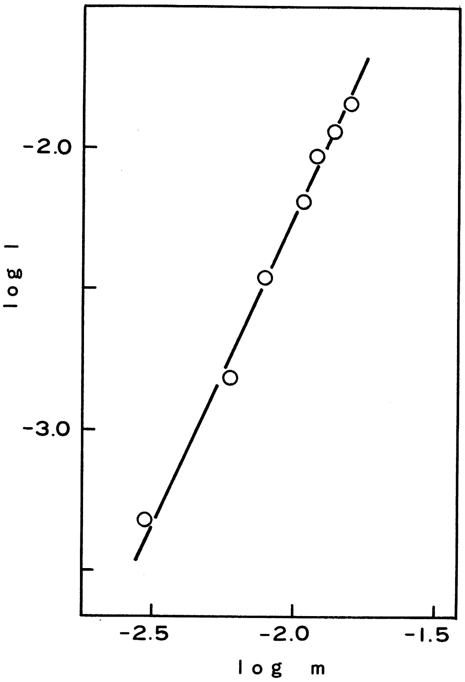

Fig. 5. Logarithmic plot for Fig. 4(b).

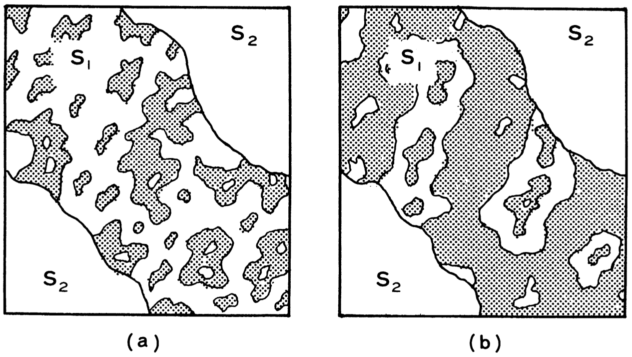

Fig. 6. Scheme for silk fibroin containing water. S_1 and S_2 indicate structure 1 and 2, respectively. The cloudy region represents the portion softened by the penetration of water.

practice, some phenomena described by this function have been successfully interpreted by employing the fractal concept [23]. On the other hand, it is generally accepted in the field of fractal science that critical phenomena such as the glass–rubber transition is characterized by the fractal figure [24].

In consideration of the discussion on glass–rubber transition and its theoretical approaches described above, and of the results obtained in the present work, we present a scheme shown in Fig. 6 for silk fibroin containing water.

The penetrating behavior of water into silk fibroin can be interpreted by employing this microscopic figure as follows. The water vapor tends to penetrate into a loosely aggregated structure S_1 prior to the densely aggregated structure S_2. The penetration of water softens the structure, and hence some portion in S_1 will transfer from glassy to rubbery (such a feature is shown in Fig. 6(a)). When the softened portion has grown into a certain critical size as shown in Fig. 6(b), silk fibroin containing water exhibits glass–rubber transition behavior. The softened portion of S_1 will sway segments of S_2 and stimulate the rearrangement of chains. The swaying is effective in the state of Fig. 6(b). It is considered that the steep increase of penetration shown in Fig. 2 reflects such a circumstance. Fig. 6(b) can be also regarded as the critical state of percolation, in other words, the figure of the softened portion is fractal. The phenomenon with fractal nature follows log–log plots. The power law held for penetrating behavior will demonstrate the fractal nature of the softened portion.

The softening behavior is interpreted as follows. The softening means an increase of mobilities of segments, that is, a decrease of relaxation times. The data of elongation shown in Fig. 4, therefore, indicates an increase of the mobilities or of the reciprocal of relaxation times caused by the penetration of water. Thus Fig. 5 can be regarded as $\log 1/\tau \sim \log s$, where τ is the relaxation time and s is the amount of sorbed water. The linear relationship means that softening by penetration of water follows the equation by Cohen and Grest ($\tau = \tau_0 S^{-k}$; $1/\tau = 1/\tau_0 s^k$). The relationship is valid above the critical point, while S_1 undergoes glass–rubber transition around the water concentration. This implies the fractal figure as shown in Fig. 6(b) for S_1 is softened by the penetration of water.

We have examined the data on the penetrating and softening behavior in consideration of the concept of fractals. The fractal structure is convenient to interpret such data. If the instrument such as the NMR microscope is available, we can directly see the change of morphology of silk by the penetration of water. Actually, the solvent diffusion in polymers has been studied by using NMR [25,26]. However, the resolving power of images is still insufficient to discuss the microscopic structure. The concept of fractal is very useful in cases where the conventional approach is powerless for the analysis of phenomena [27].

In recent years we have seen noteworthy developments in both theory and experiments for amorphous polymers. On the other hand, the need of new ideas or concepts for the elucidation of problems has been emphasized by various investigators [28,29]. Fractals will be suitable for understanding of complex structure of silk fibroin.

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