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Probabilistic Model for the Structure of the Microfibril of Cellulose

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Synopsis

A probabilistic model is presented for the structure of an "ideal" microfibril of cellulose and the distribution of weak bonds along this microfibril is calculated. Exact and asymptotic formulas are derived for the number and weight distributions and for the corresponding averages. The relationship is examined between the model of Kuhn, accepted in theory of random degradation of chain polymers, and the probabilistic model which describes the structure of the ideal microfibril of cellulose.

Introduction

The purpose of this article is to present a probabilistic model for a certain hypothesis concerning the structure of the microfibril of cellulose.[1,2] We should note, however, that we are concerned with an "ideal" microfibril and we do not intend to consider how closely the ideal microfibril approximates the actual one.

According to the hypothesis, the structure of the ideal microfibril resembles that of a brick wall. Let us visualize a monomer having the shape of a cube with a side length of unity, and let us consider a chain molecule having N links (monomers) as a brick of length N. Let us call a combination of p bricks of this kind, with their square faces touching each other, a "row" of length pN (See Fig. 1, where $N = 5$, $p = 3$).

One may regard a microfibril of length pN as a union of a certain number, m, of such rows (see Fig. 2, where $m = 9$).

In a real wall the cement is found between any two adjacent bricks which belong to the same row as well as between any two adjacent bricks belonging to different rows. It is also usually the case that when two bricks belonging to different rows touch each other the end of one will coincide with the middle of the other. For the structure of the microfibril, however, we shall assume that (*a*) the cement is found only between two adjacent bricks which do not belong to the same row, while bricks which belong to the same row are not cemented together; (*b*) the mutual position of two bricks which touch each other and belong to different rows is random in the following sense: denote by $0, 1, \ldots, N-1$ the ends—say the left-hand ones—of each of the monomers of which the brick A is composed. Then the left-hand end of brick B—which touches A but does not belong to the same

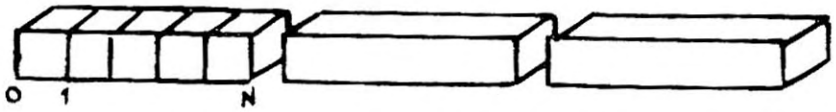

Figure 1.

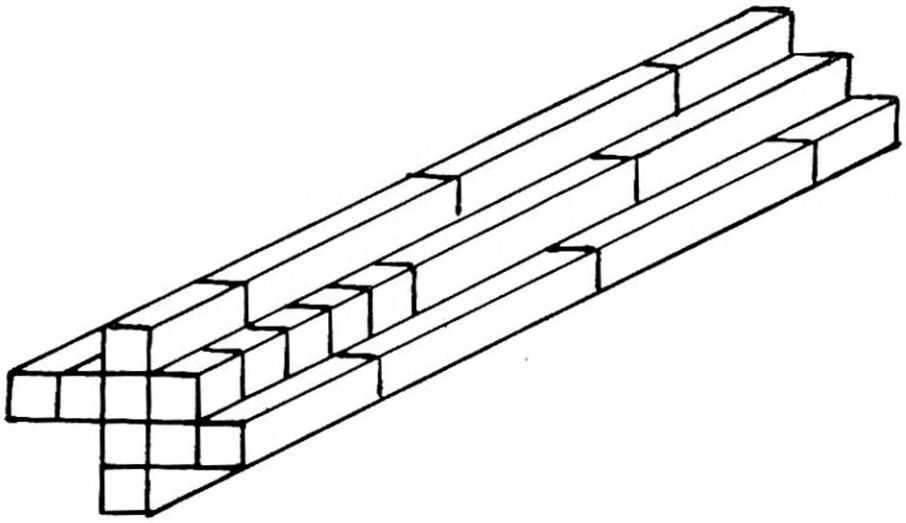

Figure 2.

row—may coincide, with equal probability, with any one of the points $0, 1, \ldots, N-1$.

On the two ends of a real wall one may find half bricks. However, in view of assumption (*b*), at the ends of the ideal microfibril there may appear various different parts of the original brick molecule. It is however clear that the length of any such part is always measured in terms of an integral number of units and that the sum of lengths of the two parts belonging to the same row is always equal to N.

Consider now a microfibril formed by a random union of m rows of length pN, according to assumptions (*a*) and (*b*) (Fig. 2). It should be noted that for our purpose the form of the cross section of the microfibril is not important at all: it could be a rectangle, square or any polygon consisting of the unit squares, i.e., of the unit square cross sections of the cube-shaped monomers.

Since the bricks within a single row are not cemented to each other [assumption (*a*)], the adjacent square-shaped sides will appear, as it were, as "cracks" in the structure. Any cross section of the microfibril which contains at least one crack in its plane will be called a "weak bond," and our purpose is to determine the distribution of weak bonds along the microfibril.

Our problem can be related to various probabilistic schemes. It seems, however, most natural to use the language which is customary in the theory of random degradation of chain polymers, since our problem, as will be seen later, is analogous to that involved in the theory of random degradation. For this reason we shall begin with a short description of one of the models of random degradation. We shall then present the probabilistic formulation of our model and develop the necessary formulas. Finally,

we shall investigate the relationship between our formulas and the corresponding ones used in the theory of random degradation of chain polymers.

Kuhn's Model

The simplest mathematical model for the purpose of describing the degradation process of chain polymers is that of Kuhn.[3] This model deals with an initial chain having $(N + 1)$ links and N bonds. The process of degradation is regarded as a sequence of random trials each of which breaks one of the bonds. It is assumed that the degradation is random, i.e., that all bonds still intact at any one stage of the degradation have the same probability of being broken.

After m trials the initial chain will be converted into $(m + 1)$ chain fragments. If we measure the length n of every chain by the number of its links, then the number distribution of the chains by their length after m trials is given by the formula[4]

$$P(n,m) = \binom{N-n}{m-1} \Big/ \binom{N}{m} \tag{1}$$

where $P(n,m)$ denotes the expected value of the relative frequency of the chains of length n after m trials. It is more common to use the weight distribution

$$F(n,m) = n \binom{N-n}{m-1} \Big/ \binom{N+1}{m+1} \tag{2}$$

where $F(n,m)$ denotes the expected value of the weight of all the molecules of length n relative to the total weight $(N + 1)$.

The "degree of degradation" is defined by the ratio

$$\alpha = \text{number of bonds broken/initial number of bonds} \tag{3}$$

Therefore, according to our notation

$$\alpha = m/N \tag{4}$$

The fact that N is usually a fairly large number enables us to use simpler formulas, which are obtained from eqs. (1) and (2) by passing to the limit $N \to \infty$ and assuming

$$\alpha = \lim_{N \to \infty} (m/N) \tag{5}$$

This leads to the formulas

$$P(n, \alpha) = \alpha (1 - \alpha)^{n-1} \tag{6}$$

$$F(n, \alpha) = n\alpha^2(1 - \alpha)^{n-1} \tag{7}$$

where $P(n, \alpha)$ and $F(n, \alpha)$ are the limiting expressions for $P(n, m)$ and $F(n, m)$.

The number-average $\bar{n}(\alpha)$ and weight-average $\bar{n}_w(\alpha)$ of the distributions (6) and (7) are given by eqs. (8) and (9), respectively:

$$\bar{n}(\alpha) = 1/\alpha \tag{8}$$

$$\bar{n}_w(\alpha) = (2 - \alpha)/\alpha \tag{9}$$

The Probabilistic Formulation of Our Model

The arrangement of the weak bonds along the microfibril can be described by the distribution of the lengths of the partial microfibrils which are obtained when we cut the original microfibril at each weak bond. We can, therefore, treat the distribution of the weak bonds as if resulting from the degradation of the original microfibril. This distribution is entirely independent of the number p of bricks in a row, because our ideal microfibril is made up of a homogeneous material, i.e., all bricks (molecules) have the same length N. It is therefore sufficient to consider the distribution of the weak bonds along one brick.

Let us consider a segment $[0, N]$, the projection of the brick as a chain of length N and the points $1, 2, \ldots, N - 1$, as its bonds. Consider now a sequence of random trials in each of which the probability of a given bond being broken is constant and equals $1/N$, in contrast to Kuhn's model, where this probability is a function of the serial number of the trial. In our model we have initially $N - 1$ unbroken bonds and one chain. A trial may or may not result in one bond being broken; if a bond is broken, the number of unbroken bonds decreases by one, while the number of chains increases by one. It follows that the sum of the number of unbroken bonds and the number of chains must remain constant and equal to N.

It is easily seen that our model reflects the structure of the ideal microfibril described in the introduction. Our purpose is to determine the distribution of chains by length and weight after m trials.

It will be noted that our model will still be valid if we consider as weak bonds only those cross sections passing through the cracks on the envelope of the microfibril, and ignore those including the cracks located in the interior. In this case m will denote the number of rows which participate in the envelope of the microfibril (and not the number of all the rows which constitute the microfibril).

Expected Value of the Number of Fragments after m Trials

In our model, unlike in Kuhn's, the number of all the chains after m trials is not defined uniquely: it is a random variable which we denote by $\mu(m)$. As a result of an additional trial, $\mu(m)$ may either increase by one unit or remain unchanged. In other words, the possible values of the random variable δ, defined by

$$\delta = \mu(m + 1) - \mu(m) \tag{10}$$

are 0 and 1. δ assumes the value 1 if and only if as a result of $(m + 1)$th trial one bond out of all bonds still intact after the mth trial is broken. Just before the $(m + 1)$th trial, however, there are $N - \mu(m)$ bonds, therefore, the probability of a bond being broken on this trial is

$$[N - M(m)]/N$$

where $M(m)$ denotes the expected value of $\mu(m)$. Hence, the expected value $E(\delta)$ of δ is

$$E(\delta) = 1 - M(m)/N$$

We obtain from eq. (10) eq. (11):

$$M(m + 1) - (1 - 1/N)M(m) = 1 \tag{11}$$

This is a linear difference equation of first order. Its general solution is

$$M(m) = C(1 - 1/N)^m + N$$

where C is a constant independent of m. Taking into account the initial conditions $M(0) = 1$, we obtain eq. (12):

$$M(m) = (N^{m+1} - (N - 1)^{m+1})/N^m \tag{12}$$

Expected Value of the Number of Fragments of Length n after m Trials

Let us denote by $\sigma(n,m)$ the random variable, number of chains of length n after m trials, and by $S(n,m)$ its expected value. As a result of one additional trial, there are only four possibilities with respect to $\sigma\ (n,m)$: it may decrease by one unit, it may remain unchanged, it may increase by one unit or increase by two units. Therefore, the possible values of the random difference

$$\delta = \sigma\ (n,m + 1) - \sigma\ (n,m) \tag{13}$$

are -1, 0, 1, and 2.

The variable δ assumes the value -1 if and only if one of the bonds of any of the $\sigma(n,m)$ chains of length n is broken as a result of the $(m + 1)$th trial. The number of all bonds of all chains of length n, which exist after the mth trial, is

$$(n - 1)\ \sigma(n,m)$$

Therefore, the probability of $\delta = -1$ is

$$(n - 1)S(n,m)/N$$

For δ to assume the value 2 a chain of length $2n$ must be broken at the $(m + 1)$th trial. Each such chain contains only one bond, the breaking of which will produce two new chains of length n each. Therefore, the probability of $\delta = 2$ is $S(2n,m)/N$.

In order to have $\delta = 1$ it is necessary to break at the $(m + 1)$th trial a chain of length k, where $k > n$, $k \neq 2n$. Each of these chains contains two

bonds, the breaking of which will produce an additional chain of length n. Therefore, the probability of $\delta = 1$ is

$$(2/N) \sum_k S(k,m)$$

where the sum runs over all natural values of k which satisfy: $n + 1 \leqslant k \leqslant N$, $k \neq 2n$.

We thus obtain for the expected value $E(\delta)$ the equality

$$E(\delta) = -\frac{(n-1)S(n,m)}{N} + \frac{2}{N}\sum_k S(k,m) + \frac{2}{N} S(2n;m)$$

In view of eq. (13) we have

$$E(\delta) = S(n,m+1) - S(n,m)$$

hence we obtain the equation

$$S(n,m+1) = \frac{N-n+1}{N} S(n,m) + \frac{2}{N} \sum_{k=n-1}^{N} S(k,m) \tag{14}$$

Thus a difference equation is again obtained. The initial conditions are

$$S(k,0) = 0 \text{ if } 1 \leqslant k \leqslant N-1;\ S(N,0) = 1 \tag{15}$$

Using eqs. (14) and (15) we can compute $S(k,m)$ successively for each k and m. It can be shown that $S(n,m)$ is given by the formulas

$$S(n,m) = [(N-n+1)^{m+1} - (N-n-1)^{m+1} - 2(N-n)^{m+1}]/N^m \quad \text{if } 1 \leqslant n \leqslant N-1$$

$$S(N,m) = 1/N^m \tag{16}$$

The formula for $S(N, m)$ is obvious: a chain of length N will be obtained after m trials if and only if in each one of these trials all $(N - 1)$ original bonds remain intact. By using the method of complete induction it can be shown that eq. (16) holds also for every n, $1 \leqslant n \leqslant N - 1$ (see Appendix).

Distribution of the Chains by Length and Weight: Exact and Asymptotic

The expected value of the relative frequency of chains of length n after M trials is defined by the formula

$$P(n,m) \cong S(n,m)/M(m)$$

(for large values of m)

Hence, by using eqs. (12) and (16) we obtain

$$P(n,m) = \frac{(N-n+1)^{m+1} + (N-n-1)^{m+1} - 2(N-n)^{m+1}}{N^{m+1} - (N-n)^{m+1}} \quad \text{if } 1 \leqslant n \leqslant N-1$$

$$P(N,m) = 1/(N^{m+1} - (N-1)^{m+1}) \tag{17}$$

APPENDIX

We shall now prove that (16) is in fact the formula which solves eq. (14) for the initial conditions (15). We may assume that $1 \leqslant n \leqslant N - 1$.

If we insert $m = 0$ in eq. (14), we obtain from (15)

$$S(n,1) = 2/N$$

for all $1 \leqslant n \leqslant N - 1$. The same result follows from eq. (16), if we insert $m = 1$.

Let us therefore assume that (16) is true for a certain m and prove that it is true for $(m + 1)$. From eqs. (14) and (16) we obtain:

$$\begin{aligned} S(n,m+1) = \frac{N-n+1}{N^{m+1}} &[(N-n+1)^{m+1} \\ &+ (N-n-1)^{m+1} - 2(N-n)^{m+1}] + \frac{2}{N^{m+1}} \\ &\times \left[1 + \sum_{k=n+1}^{N-1} (N-k+1)^{m+1} \right. \\ &\left. + \sum_{k=n+1}^{N-1} (N-k-1)^{m+1} - 2\sum_{k=n+1}^{N-1} (N-k)^{m+1}\right] \end{aligned} \tag{26}$$

If we assume $N - k + 1 = t$, we have

$$1 + \Sigma_1 = 1 + \sum_{k=n+1}^{N-1} (N-k+1)^{m+1} = 1 + \sum_{t=2}^{N-1} t^{m+1} = \sum_{t=1}^{N-1} t^{m+1}$$

Similarly we obtain

$$\Sigma_2 = \sum_{k=n+1}^{N-1} (N-k-1)^{m+1} = \sum_{t=1}^{N-n-2} t^{m+1}$$

$$\Sigma_3 = \sum_{k=n+1}^{N-1} (N-k)^{m+1} = \sum_{t=1}^{N-n-1} t^{m+1}$$

Hence

$$1 + \Sigma_1 + \Sigma_2 - 2\Sigma_3 = (N-n)^{m+1} - (N-n-1)^{m+1}$$

Therefore, using eq. (26), we obtain, after elementary transformations,

$$S(n,m+1) = [(N-n+1)^{m+2} + (N-n-1)^{m+2} - 2(N-n)^{m+2}]/N^{m+1}$$

which is identical with eq. (16), if $(m + 1)$ is substituted for m.

The present mathematical treatment has been suggested to me by the chemical research conducted by Dr. I. Ohad[6] of the Department of Biological Chemistry of Hebrew University of Jerusalem.

I wish to express my thanks to Dr. M. Lewin, Director of Research of this Institute, for his continuing interest in this work.

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Résumé

On présente ici un modèle probable pour la structure d'une microfibrille de cellulose 'idéale' et on a calculé la distribution des liens faibles le long de cette microfibrille. On a obtenu des formules exactes et asymptotiques pour la distribution en nombre et en poids ainsi que pour les moyennes correspondantes. On a examiné la relation entre le modèle de Kuhn, accepté dans la théorie de la dégradation statistique des chaînes polymériques, et le modèle le plus probable qui décrit la structure d'une microfibrille idéale de cellulose.

Zusammenfassung

Ein Wahrscheinlichkeitsmodell für die Struktur einer "idealen" Zellulosemikrofibrille wird aufgestellt, und die Verteilung schwacher Bindungen in dieser Mikrofibrille wird berechnet. Exakte und asymptotische Beziehungen für die Zahlen- und Gewichtsverteilung und für die entsprechenden Mittelwerte werden abgeleitet. Die Beziehung zwischen dem in der Theorie des statistischen Abbaus von Kettenpolymeren angenommenen Modell von Kuhn und dem Wahrscheinlichkeitsmodell, welches die Struktur der idealen Zellulosemikrofibrille beschreibt, wird untersucht.

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