

# Static Intermolecular Slipping of Crude Rubber by Stretching

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## Abstract

The amount of static intermolecular slipping which occurs during the storage at room temperature of a ribbon of crude rubber in a stretched state was calculated on the assumption that the time rate of decrease of the actual degree of stretching is proportional to the amount of the uncrystallized amorphous part and also to the actual degree of stretching which is really acting as a contractive tension in the amorphous part; and the result of calculation agreed, in general, with results obtained by observation.

The ease of stretching a crude rubber ribbon suddenly without breaking, up to the stretching degree of more than 6-fold, was explained by the hooking effect between molecules in the part crystallized by stretching, which acts to prevent further slipping in the more crystallized part having initially a smaller cross section.

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It was observed by one of the writers that when a ribbon of crude rubber was stretched suddenly and kept for some time in the stretched state, intermolecular slipping took place during storage in the stretched state. The amount of the slipping was measured by making the specimen contract rapidly by dipping it in boiling water for about 10 minutes after the release of the stretching tension, and then measuring the increase of its length in comparison with its original unit length. The slipping increases with the temperature and the duration of its storage in a stretched state. With respect to the stretching degree, it was found that the slipping increases at first with increase of the stretching, attains a maximum at the stretching of about 2-3 fold, then decreases to a constant value of 0.125 at the stretching of about 5.2-fold. This constant value of the slipping is the same for all stronger stretchings up to 7-fold. Also it is not affected by continued storage in the stretched state, and remains the same as when measured immediately after the sudden stretching, and the slipping has evidently arisen in the process of sudden stretching. As the crystallization of the rubber molecules in a fibrous manner is almost complete when the stretching is higher than about 5-fold, the

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1. C. Park: These Memoirs, **23** (1940).

sudden decrease of the intermolecular slipping on further stretching is thought to be caused by a kind of hooking effect between the molecules of rubber when arranged in a crystal lattice. On this assumption, it seems reasonable to suppose that the intermolecular slipping occurs only in the uncrystallized amorphous portion, and not in the crystallized part, and it increases with the actual degree of stretching which, in the amorphous part, acts as a contractive tension. This furnishes a reasonable qualitative explanation of the relation observed between the degree of slipping and the degree of stretching, namely that up to a certain point the slipping increases with the increase of stretching, but finally, having reached a maximum, it falls.

It was also reported by one<sup>1</sup> of the writers that when the stretching process was made continuously and very slowly, the amount of intermolecular slipping was enormous as compared with that observed with quick stretching and prolonged storage in the stretched state. In analogy with the kinetic and static friction between the surfaces of two solids, he called the intermolecular slipping occurring in the process of continuous and slow stretching "kinetic intermolecular slipping" and that occurring during storage in the stretched state of the specimen stretched quickly "static intermolecular slipping." Following the suggested explanation of the intermolecular slipping, a simple calculation was made with the data obtained by one of the writers, for the case of static intermolecular slipping at room temperature.

The intermolecular slipping at any moment during storage in a stretched state must be considered to depend upon the actual degree of stretching which is really acting as contractive tension for the specimen at that moment. The actual degree of stretching is different from the degree of stretching imposed on the specimen initially by stretching, and to obtain the actual degree of stretching at a given moment, the initial degree of stretching must be corrected to cover the amount of slipping that has taken place during the period of storage. In considering the change in the amount of slip with the time of storage in the stretched state the initial condition, that is the state just after the quick stretching must be carefully observed. Some slight slipping is found to have taken place even just after the sudden stretching, and this must be considered to have happened during the stretching process. If a ribbon of rubber of the length  $l_0$  is stretched

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1. Ibid

suddenly to the stretching degree  $S_0$ , and is allowed immediately to contract as completely as it will by dipping it in boiling water for about 10 minutes after the release of the stretching tension, the contracted length  $l'_0$  is found to be somewhat longer than the initial length  $l_0$  due to the intermolecular slipping which took place with the process of stretching. Thus the actual stretching degree  $S'_0$  just after the momentary stretching will be represented by the formula :

$$l_0(1 + S_0) = l'_0(1 + S'_0) = L_0 \dots\dots\dots(1)$$

where  $L_0$  is the stretched length.

From the values of  $l'_0$  observed by one of the writers (C. Park), the actual stretching degree  $S'_0$  just after the stretching, was calculated and is given in Table I.

Table I

$S_0$	1.5	2.5	3.5	4.5	5.2	7.0
$\frac{l'_0}{l_0}$	1.05	1.10	1.12	1.12	1.125	1.125
$S'_0$	1.38	2.18	3.02	3.91	4.52	6.12

Now let a rubber ribbon of the length  $l_0$  be stretched momentarily to a certain degree and stored for a certain duration in the stretched state, then

this length  $l_0$  becomes elongated to the "free length"  $l_f$  when it is entirely set free from its stretching tension by being dipped in boiling water after the removal of the stretching tension.

As this is caused by the intermolecular slipping the ratio  $l_f/l_0$  or more exactly  $l_f/l'_0$  can be considered to be a measure of intermolecular slipping occurring during the storage of the specimen in a stretched state. Thus if we represent by  $S$  the actual degree of stretching working really as a contractive tension in the specimen after it has been stored for a duration of time  $t$  in a stretched state, the relation between  $S$  and the free length  $l_f$  at that moment will be given by the formula

$$l'_0(1 + S'_0) = l_f(1 + S) = L_0 \dots\dots\dots(2)$$

As before stated intermolecular slipping does not occur during storage in a stretched state at a stretching higher than about 5.2-fold where the fibrous crystallization is not far from completion. With the stretching lower than this critical value some part of the specimen is, of course, crystallized ; and the degree of crystallization increases with the degree of stretching. Since it is reasonable to suppose that in this case also the intermolecular slipping does not occur in the almost crystallized part, we shall assume that the intermolecular slipping takes place only in the amorphous part, and that the slip increases with

the real degree of stretching acting as a contractive tension in this part.

The proportion of the amorphous part to the whole of the specimen decreases with the increase of the stretching degree, and we shall assume roughly that it decreases linearly with the actual stretching degree. As the crystallization is almost complete with a stretching degree higher than about 5.2, (which corresponds to the actual stretching degree 4.52 just after the stretching) the proportion of the amorphous part, which is assumed to be proportional to the slip occurring in unit time, thus becomes

$$\frac{4.52 - S}{4.52},$$

In regard to the relation between the intermolecular slipping and the degree of stretching, the former seems not to take place with a very small stretching, say less than about 0.15. Therefore we assume that the slip occurring in unit time is proportional to  $S - 0.15$ .

When intermolecular slipping occurs, the actual degree of stretching which is working as a contractive tension decreases. Consequently by taking, in the following equation, the amount of decrease of the actual stretching degree per unit time as a measure of the amount of the slip occurring in unit time, we get

$$-\frac{dS}{dt} = \frac{\beta}{4.52} (4.52 - S)(S - 0.15), \dots \dots \dots (3)$$

where  $\beta$  is a proportional factor and  $t$  is the time of storage of the specimen in a stretched state commencing from the moment just after the initial stretching process.

Equation (3) becomes on integration

$$\frac{S - 0.15}{4.52 - S} = \frac{S_0' - 0.15}{4.52 - S_0'} e^{-\beta' t}, \dots \dots \dots (4)$$

where  $\beta'$  is a new constant equal to

$$\frac{4.52 - 0.15}{4.52} \beta.$$

By writing

$$X = \frac{S - 0.15}{4.52 - S}, \quad X_0 = \frac{S_0' - 0.15}{4.52 - S_0'},$$

we get from equation (4)

$$X = X_0 e^{-\beta' t} \dots \dots \dots (5)$$

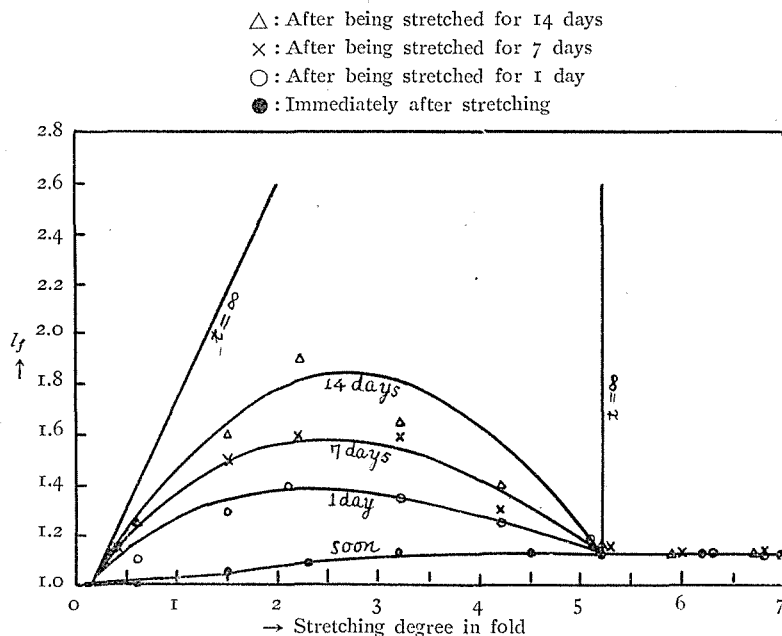
If we take the logarithm of both sides of equation (5) we have

$$\log_{10} \left( \frac{X}{X_0} \right) = -\beta' t \log_{10} e \dots \dots \dots (6)$$

The value of  $S$  and consequently  $X$  can be calculated by means of equation (2) for various values of  $S_0'$  and  $t$ ; and by plotting the relation between  $\log_{10}(X/X_0)$  and  $t$ , it was found that the value  $\beta'$  was much greater in storage for less than one day than after longer storage. This larger slipping seems to be due to a worse settling of the molecular arrangement in the early stage of the storage of the specimen just after the stretching, and this may be of the same nature, at least to some extent, as kinetic slipping which takes place during slow and continuous stretching. For the storage for one day the value of 0.616 was adopted for  $\beta'$ , and for the longer storage the value of  $X_1$  for one day as calculated with equation (4), was made as the initial value of  $X$ , which corresponds to  $X_0$  in equation (5), and the value of 0.062 was given to  $\beta'$ .

In this way the values of  $S$  and consequently the values of  $l_f$  corresponding to various values of initial degree of stretching  $S_0'$  and the duration of storage  $t$  were calculated by means of equations (4) and (2), and the results are shown by the curves in Fig. 1. In these curves the one called "soon" represents the free length just after the stretching, and those marked  $t=\infty$  are the values calculated for the

Fig. 1



infinite duration of storage where the actual degree of stretching disappeared almost entirely, except the very small value of 0.15 below which no intermolecular slipping is supposed to take place. In the figure the observed values of free length  $l_f$  are shown by dots, small circles, crosses and small triangles respectively for immediately after stretching, one day's storage, 7 days' storage and two weeks' storage. Though the agreement between the calculation and the observation is not perfect, the general tendency of the figure seems to support the view adopted in constructing the differential equation for the intermolecular slipping in the stretched state.

Lastly the writers will consider a very interesting phenomenon which we always experience when stretching a ribbon of crude rubber very slowly and continuously. With stretching so slow as to take several hours to stretch the ribbon to several-fold of its original length, it is almost impossible to stretch it longer than about 2- or 3-fold, where it breaks down even with a ribbon of apparently uniform cross section. This is entirely different from the case of sudden stretching, where it is always possible to stretch even up to 7-fold without breaking. Even with a ribbon of apparently uniform size, we must always expect some lack of uniformity of the cross section. In stretching such a ribbon quickly to more than about 4- or 5-fold, the portion having smaller cross section will be more elongated, and consequently it will be so nearly crystallized as to be rescued from further intermolecular slipping the hooking effect. Contrary to the case in the portion with smaller by cross section, the intermolecular slipping will be greater in the part of greater cross section due to the weaker hooking effect corresponding to the weaker stretching and the consequent smaller degree of crystallization. Thus the quick stretching to a very high degree acts rather to minimize and never to increase, that tendency to destroy the uniformity of the cross section, which is the cause of the break of the specimen. Next when a rubber ribbon is stretched very slowly and continuously, kinetic slipping of an enormous amount takes place, hindering the specimen from being so stretched as to have enough contractive tension to make the crystallization, and consequently the hooking effect, noticeable. In such a case intermolecular slipping is greater in the part of smaller cross section, where the actual degree of stretching is higher than in the part of larger cross section. With increasing stretching and slipping, the part with the smaller cross section, lacking as it does the hooking effect, becomes increasingly thinner than the part

with greater cross section until the break takes place at that part before the specimen is stretched sufficiently. This is the phenomenon well known in the case of tensile testing of ordinary materials.

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