

Second Report of the Investigation on the Crystallization of Crude Rubber

By Chullchai Park (朴哲在)

(Received June 16, 1939)

Abstract

When a stretched ribbon of crude rubber is frozen at a temperature below about 0°C , a small elongation arises in the stretched direction. Such small elongation was measured with various degrees of stretching and after freezing at the very low temperature of -40°C , and the results were compared with those obtained previously by freezing at about -5°C . When a slightly stretched rubber ribbon is frozen, the fibre diagram obtained by X-ray diffraction becomes very sharp and clear. This point was re-examined minutely with various degrees of stretching. The changes of the density of rubber by stretching and by freezing at various temperatures were measured, and it was found that the density increased with increasing degree of stretching and with decrease of the freezing temperature. By cooling a thin ribbon of crude rubber from room temperature to about -70°C suddenly, hard, transparent and amorphous rubber ribbon was obtained as its super-cooled state; and it was observed that the super-cooling of crude rubber happens by cooling suddenly to a temperature lower than about -35°C . Lastly a diagrammatic representation of the transformation of rubber from amorphous to crystalline state and vice versa is proposed.

Introduction: Very recently¹ the writer observed a small elongation of a stretched ribbon of smoked sheet of rubber in the stretched direction by freezing, and it was found that the maximum elongation occurred with the stretching of about 200–300 percent of the original length, and also that almost no elongation took place with stretching higher than about 700 percent. To explain the behaviour of the crude rubber by crystallization, including these facts, it was assumed that the long chain molecules of rubber are in the form of large irregular spirals.

Elongations by freezing of stretched ribbons of rubber: In the present experiment, the writer first measured the small elongations of smoked sheet ribbons of rubber stretched differently, which were caused by freezing at the temperature of about -40°C . The results are tabulated in Table I. In this table the stretching is represented in percentage of the ratio of the stretched length to the initial unstretched length, and the elongation by freezing of the specimen is expressed in percentage of the stretched length.

1. C. Park: These Memoirs, **22**, 13 (1939).

Table I

| Stretching in % | Not stretched | 200 | 300 | 400 | 500 | 600 | 700 | 800 |
|--------------------------------|------------------------|-----|-----|-----|-----|-----|-----|------------------------|
| Elongation by freezing in % | difficult to detect | 2 | 3.5 | 4 | 3 | 2 | 1 | difficult to detect |

With a freezing temperature of about -5°C , at which the previous experiment was performed, the maximum elongation occurred with a stretching of about 200–300 percent of the original length and there was almost no elongation with stretching higher than about 700 percent. However, with a much lower freezing temperature of about -40°C , the position of the maximum elongation by freezing moved to the stretching of about 400 percent, and a little elongation of about 1 percent was still detected at the severe stretching of about 700 percent as shown in Table I.

Change of the X-ray diffraction pattern, by freezing, of a stretched ribbon: It is reported in the previous paper that when a ribbon of rubber kept slightly stretched in an uncrystallized degree is frozen it gives an imperfect fibre diagram by taking the direction of stretching as its fibre axis. This point was re-examined more minutely in the present experiment, by using the same freezing camera as was used before which was especially suited to keep the specimen frozen during the whole exposure of the photographic plate to the diffracted X-rays. With a ribbon of smoked sheet of rubber, which was stretched 200 percent, it gave only a diffuse amorphous halo at room temperature as shown by Fig. 1a in Plate I, but when frozen in the stretched state at about -20°C , it gave a fibre diagram of mediate intensity superimposed on the background of the diffuse halo much diminished in its intensity as shown by Fig. 1b of Plate I. With a ribbon stretched 300 percent, a very faint fibre diagram at room temperature became sharp and very intense by being frozen at about -20°C with the same exposure, as is seen by comparing the two diffraction photographs reproduced in Figs. 2a and 2b of Plate I. The diffuse amorphous halo almost disappeared in this case. With a high degree of stretching such as 800 percent, the crystallization of the rubber molecules in the fibrous manner is almost completed even at room temperature, and any further accomplishment of crystallization by freezing could scarcely be detected as shown in Figs. 3a and 3b of Plate I. These facts seem to show that the tolerably straightened but still not crystallized chain molecules of rubber, which exist in large numbers in low stretch-

ed ribbon, fit together to form a crystal lattice of aligning fibre form by freezing, and that this is the cause of the occurrence of a small elongation in the stretched direction by freezing and moreover that the major part of the rubber molecules are already arranged at room temperature in a crystal lattice in the fibrous manner with high degree of stretching, resulting in no more crystallization and no more elongation in the stretched direction by freezing.

The lengths of the short arcs of the diffraction spots due to an imperfect fibrous arrangement of the rubber molecules which was caused by stretching were measured roughly and plotted in Fig. 1 in reference to the stretched degree. In doing so, the most intense spots A_1 (200), A_2 (002) and I_2 (012)¹ were chosen. In taking the diffraction photographs the distance between the sample and the plate was 3.65 cm and the diameter of the circular slit was 0.12 cm and these were kept the same throughout the present experiment. As the length of each arc of the diffraction spots remained the same at room temperature for various degree of stretching, the arc length of the spot A_2 (002) obtained at room temperature was taken as unity, and the arc lengths of the other spots obtained in different conditions were measured with this standard. Fig. 1a is the case obtained at room temperature. Each length of the short arcs of A_1 , A_2 , and I_2 remained approximately the same indifferently to the degree of stretching; but in Fig. 1b, which was obtained by freezing the specimen at -20°C , the arc lengths of the spots increase gradually from the normal values with the decrease of the stretching degree below about 500 percent. This seems to be due to the fact that, at a low stretching degree somewhat straightened but not crystallized chain molecules of rubber whose alignment in the stretching direction is poor, unite together by freezing to form crystallites. Consequently the alignment of the crystallites in the stretching direction becomes worse with decrease of the stretching degree. Contrary to this case the arc lengths of the diffraction spots obtained at room temperature remained roughly the same irrespective of the stretching degree as is stated before. This seems to show that the unification to the crystal lattice of the molecules of stretched rubber at room temperature occurs only among those whose alignment in the stretched direction is rather perfect.

All the experimental results as stated above seem nothing but the

1. W. Lotmar and K. H. Meyer: *Monatsch.*, **69**, 115 (1936).

Fig. 1a.
at room temperature

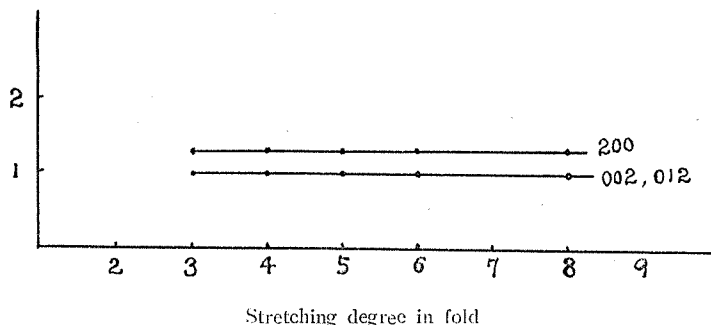
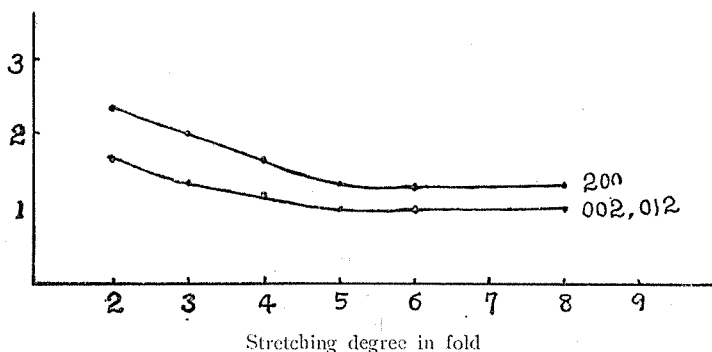


Fig. 1b.
at -20°C



support to the theory of crystallization of crude rubber, which was proposed by the writer.¹

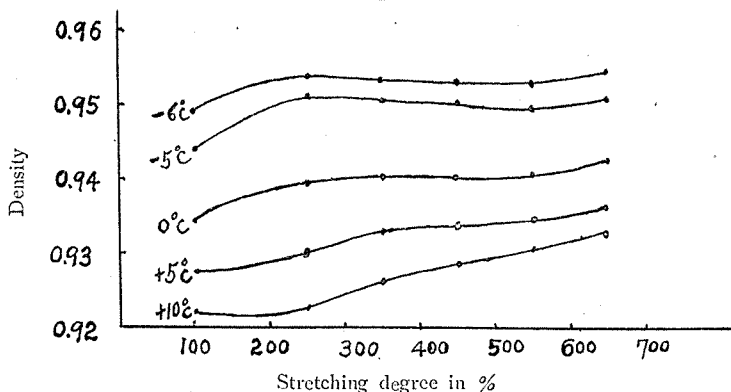
Change of density by freezing: Next the writer measured the change by freezing of the density of rubber ribbons of smoked sheet stretched in various degrees. For this purpose a special pycnometer having a long neck provided with a scale was used. This scale served to measure the change of the volume by cooling of ethyl alcohol which was contained in the pycnometer together with a stretched specimen of rubber. The stretching of a rubber ribbon was performed by fastening it to a metal wire. Essentially the change of the density of stretched rubber by cooling is to be measured by the difference between the thermal expansions of the stretched rubber and of the ethyl alcohol into which the rubber specimen is dipped. The expansion coefficient of

1. C. Park: *Loc. cit.*

ethyl alcohol 99.5% pure was measured with the pycnometer; the volume of the metal wire to which the rubber specimen was to be fastened by stretching was calculated from its mass and density, the volume at a standard temperature of the rubber ribbon which was stretched to some degree by fastening it to the metal wire was obtained from its mass and the weight measured by dipping it together with the stretching wire into ethyl alcohol at the standard temperature. The change of volume of ethyl alcohol containing the stretching wire alone was measured by changing the temperature from the standard one by a certain degree, and then the change of volume of ethyl alcohol containing the stretched ribbons of rubber together with the stretched wire was measured by changing the temperature from the standard value by the same degree as above. From such measurements the volume of the stretched specimen of rubber at a certain temperature was calculated, and consequently the value of its density at that temperature was obtained from its mass.

From the procedure described above, the writer measured the density of smoked sheet rubber in unstretched and stretched state at temperatures between $+10^{\circ}\text{C}$ and -6°C and the results are shown in Fig. 2. As will be seen from the curves in Fig. 2 the density of rubber increases with decrease of the temperature; and this tendency is especially prominent between 0°C and -6°C , where the crystallization by freezing is remarkable. As to the relation between the density and the stretching degree, the former increases with increase of the latter at a comparatively high temperature; but at a low temperature of -5°C or -6°C , where the crystallization easily occurs merely by freezing without stretching, the density remains almost the same for

Fig. 2.



different stretching. These facts seem to indicate that a remarkable change of density of rubber, which is observed in the present experiment, is mainly due to the crystallization of rubber molecules by stretching and by freezing.

It has already been stated that when a rubber ribbon, stretched to some extent, is frozen, a small elongation happens in the direction of stretching; and this elongation was attributed to the straightening and the alignment of the chain molecules of rubber to form a crystal lattice mostly in the stretched direction. As the density of rubber increases in this case as is stated above, a considerable amount of lateral contraction must be considered to happen simultaneously with a small elongation in the direction of stretching, by freezing. This is in fair agreement with the view that the small elongation in the stretched direction, caused by freezing, is due to the straightening and alignment of the chain molecules of rubber to form a crystal lattice mostly in the stretched direction.

Super-cooling of rubber: When a piece of crude rubber is kept at a temperature lower than about 5°C for some time, it becomes gradually hard and loses its transparency and elasticity and its density increases. Such rubber is usually called "frozen".

The writer immersed a piece of smoked rubber sheet suddenly into liquid air or into a cooling mixture of dry ice and acetone whose temperature was about -70°C . Unexpectedly to the writer, the piece of rubber became very hard momentarily just like a piece of metal but it retained perfectly the transparency which is peculiar to its amorphous state. This state continues long with continued cooling, and no change was detected even after two days. Next such a hardened piece of rubber was examined with X-rays by keeping it cooled continuously below about -40°C after the sudden cooling to about -70°C , and it was confirmed that the rubber was still amorphous and not crystallized in this hardened state. This is entirely analogous to the super-cooled state of a liquid, and this super-cooled state of crude rubber always obtained when its narrow ribbon was dipped suddenly into a cooling mixture of a temperature below about -35°C . When the temperature of the cooling mixture was higher than about -35°C , super-cooled state was difficult to obtain and an ordinary frozen i. e. crystallized state was usually developed. As is considered before, the fitting of the chain molecules of rubber into the lattice of the rubber crystal is caused primarily by their straightening and alignment in a same parallel direction. Thus when a piece of crude rubber is suddenly cooled to such

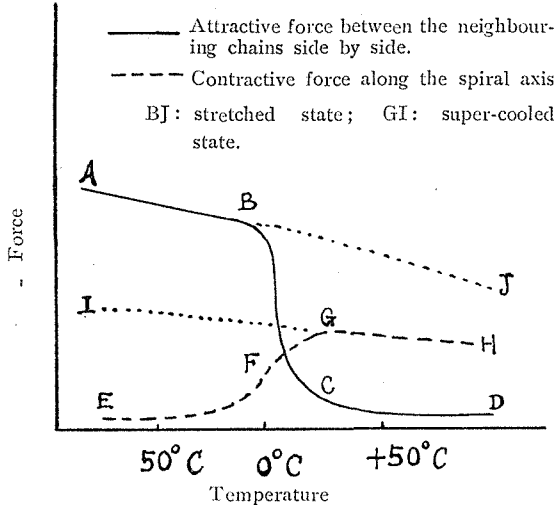
a low temperature as below -35°C , micro-Brownian movements of every part of the long chain molecules of rubber are so much weakened suddenly that the straightening and the alignment which are necessary for crystallization can no more take place; and consequently the chain molecules of rubber cohere tightly by sudden and severe cooling in an amorphous way just as they were at room temperature before cooling.

As to the density of the super-cooled specimen of smoked sheet rubber, the writer measured it roughly by immersing a super-cooled specimen into ethyl alcohol contained in a long necked pyknometer which was cooled to about -70°C , and by measuring the volume of the super-cooled specimen from the increase of volume of the ethyl alcohol. The value of the density thus measured was about 0.91-0.92 at about -70°C , and was found to be of the same order as that at room temperature. This fact indicates that a remarkable increase of the density of crude rubber by freezing and stretching as was mentioned before is mainly due to the transformation from an amorphous to a crystalline state. Super-cooling of rubber as was observed above seems to be very interesting when looked at from various view points, and a more detailed investigation is now going on.

A diagrammatic representation of the crystallization of rubber:

The crystallization of rubber is very complicated; it crystallizes by cooling and by being stretched or by being strained in some other way. An exact understanding of such complicated phenomena will be of course very far from our reach; but a general grasp, even though it is rough, is very useful in getting at the truth, so far as it is consistent in its main features. In the former paper* the writer proposed a model of rubber molecules having the shape of a large, irregular spiral, and their unification in crystallizing was supposed to be caused primarily by their straightening and alignment in the same parallel direction. Thus the crystallization and the melting were explained by comparing the attractive force between the neighbouring chain molecules side by side and the contractive force along the axis of the large irregular spiral of the rubber molecule. In Fig. 3, how these forces change with temperature is shown qualitatively with the curves drawn in full and broken lines respectively. At a temperature higher than freezing one the attractive force between the neighbouring chain molecules side by side is inferior to the contractive force along the spiral axis; however when the temperature is lowered below freezing one the former force becomes remarkably stronger than the latter, and the crystallization by freezing happens in this temperature range.

Fig. 3

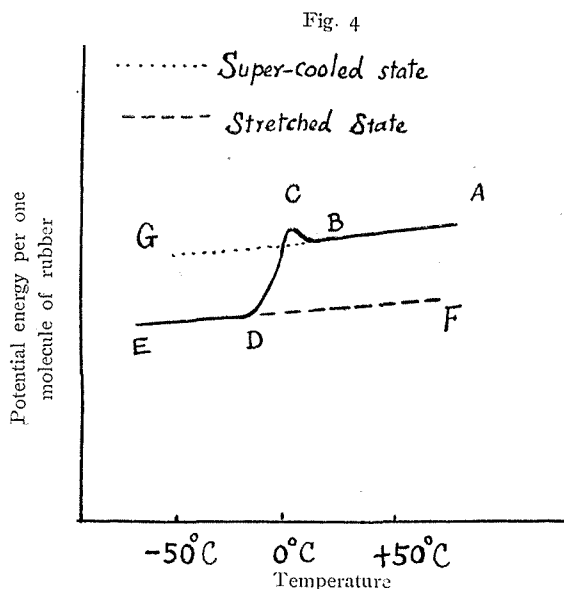


Thus the transition from amorphous to crystalline state or vice versa occurs at the point F where two curves AB-FCD and EFGH cross each other. When a rubber ribbon is stretched sufficiently, i. e. to about 8 times its original length at a temperature above freezing temperature, the contractive force along the spiral axis is compensated with the force applied

externally by stretching, leaving only the attractive force between the neighbouring chains side by side to act to crystallize in a fibrous manner. The crystallizing force in this state is shown by the dotted line BJ in Fig. 3 as the continuation of the frozen state AB. Next when a thin ribbon of rubber is cooled suddenly to such a low temperature as below about -35°C , the spirals of the rubber molecules have no time to be straightened and to fit into the crystal lattice themselves, so that the crystallization is surpassed by the amorphous state down to the lowest temperature to which it is cooled, and remains so for a long time in consequence of the want of the thermal agitation necessary for it to crystallize. The contractive force along the spiral axis in such super-cooled state is represented by the curve GI, which is drawn by a dotted line as the continuation of the curve HG. The attractive force between the neighbouring chains side by side is of course much smaller than the contractive force along the spiral axis in this case.

Let us suppose roughly that the potential energy of a rubber molecule consists of two kinds: One, that of the contractive force along the spiral axis of the rubber molecule, and the other that of the attractive force between the neighbouring chains of the rubber molecules side by side. In Fig. 4 such potential energy per molecule of rubber is considered in relation to the change of temperature, and this is represented qualitatively by a curve drawn in full line. In this curve the part AB corresponds to the amorphous state above the freezing tem-

perature, and the part DE corresponds to the crystallized state below the freezing temperature; and the transition from the amorphous state to the crystallized state is considered to occur along the part BCD. The presence of a small maximum at the point C is due to the increase of the potential energy by the rubber molecules being straightened



before crystallization. As is well known the transformation of rubber from amorphous to crystalline state and vice versa by change of temperature is accompanied by a considerable time-lag and hysteresis; and the phenomenon of super-cooling as is stated before is nothing but an extreme case of such time-lag and hysteresis. The occurrence of such remarkable time-lag and hysteresis in the process of transformation seems to be well understood by the presence of a small maximum at C in the potential curve drawn in Fig. 4, because to overcome that maximum that is to be straightened chain molecules of rubber a considerable amount of kinetic energy due to the micro-Brownian movement in the molecules is necessary. Lastly as to the crystallization by sufficient stretching at a temperature above the crystallization temperature, it seems natural to consider that the potential energy increases gradually with temperature as the continuation of the part ED of the potential curve, as is represented by the curve DF in the figure, because any remarkable indication of the change of phase in the stretched i. e. crystallized rubber is not detected on passing the crystallization temperature.

In conclusion, the writer wishes to express his sincere thanks to Professor U. Yoshida for his kind guidance and invaluable suggestions during the course of his research. His hearty thanks are also due to Assistant Professor Dr. K. Tanaka and Dr. S. Shimadzu for the facilities afforded to him during the present experiment.

Chullchai Park

Plate I

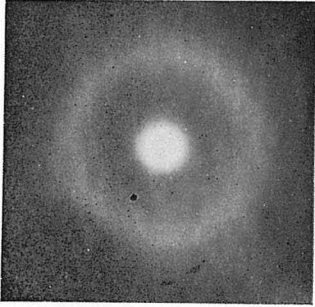


Fig. 1a

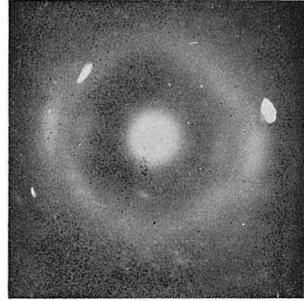


Fig. 1b

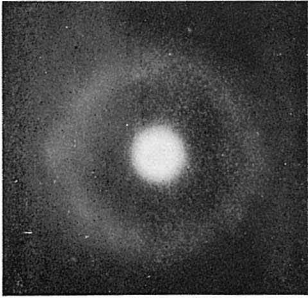


Fig. 2a

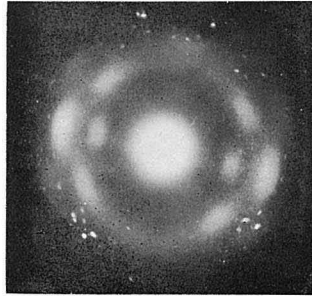


Fig. 2b

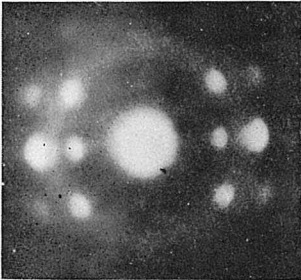


Fig. 3a

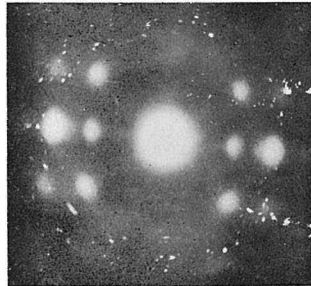


Fig. 3b