

# Modern interpretation on the high-stretching of natural rubber attained by the classic ‘racking’ method

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## Abstract

To investigate the mechanism of high elongation of natural rubber attained by the ‘racking method’, a strip of smoked-sheet was elongated up to 150 times in length, by stretching rapidly at room temperature and forcing to shrink at 75–80 °C repeatedly. On X-ray diffraction, a typical fibre pattern with an amorphous ring appeared already at  $\times 10$  (stretch ratio = 10). The degree of crystallinity increased to the level of 17–18% at  $\times 20$  and turned to decrease after  $\times 60$ , but the degree of crystallite orientation reached at a high level already at  $\times 10$  and did not change significantly and the half-height width of reflection profiles stayed almost at a constant level, while the Young’s modulus increased up to ca. 300 MPa at  $\times 100$  and then fell rather discontinuously. It was assumed that some fractions of chain segments between entanglements were gradually broken in each step of stretching operation, rather than disentangled and slipped.

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## 1. Introduction

Before synthetic polymers emerged in 1930s, natural rubber was extensively studied not only as a unique elastic material but also as a crystalline polymer. It was already known that the linear polymer consisting of poly-*cis*-isoprene tended to crystallise at low temperature, viz. in a stretched state, as recognised from its X-ray fibre pattern [1]. The crystallisation behaviour caught more attention when the characteristic mechanical properties of vulcanised rubber, namely at high stretching, were ascribed to the so-called stress-induced crystallisation [2,3]. This phenomenon has been studied further in recent years at molecular level, by employing such modern techniques as time-resolved X-ray analysis [4] and high-resolution transmission electron microscope/electron diffraction [5,6].

For synthetic polymers, it has been established during the

last few decades that a flexible linear polymer can be processed into a super-strong fibre, once a high molecular orientation is given, as such a high Young’s modulus as  $>100$  GPa was attained by the drawing of  $>\times 100$  with ultra-high-molecular polyethylene (UHMWPE) [7]. Much earlier, it was recorded in an old literature of 1920s that a smoked-sheet of natural rubber was successfully elongated up to one hundred times by what was called the ‘racking method’ in which a strip of rubber was stretched quickly by hands at room temperature and then forced to shrink in hot water repeatedly for a number of times, turning the elastic substance into a stiff rod [8,9]. It was inevitable at that time when modern analytical instruments were yet to be available that almost no details were clarified with regard to the structural change, save that crystallites were oriented as observed on an X-ray diffraction photograph. Apparently, even the stress–strain properties were not measured either.

As an approach to prepare highly oriented rubber, the classic racking method has been traced to investigate the mechanism of elongation as well as the structure and mechanical properties of stretched specimens.

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## 2. Experimental

### 2.1. Material and stretching method

The material used was a smooth-surface smoked-sheet specially prepared and supplied by courtesy of PT Perkebunan VIII Rubber Plantation, Cikumpai, West Java. The sheet, of 2.5 mm thickness, was cut into a strip of 5 mm width for subjecting to the ‘racking’. According to the description of Feuchter, the strip was first (1) stretched rapidly by hands at 20–25 °C, (2) allowed to relax at room temperature for 1 min, (3) forced to shrink by dipping in hot water of 75–80 °C and (4) stretched again as above, and the procedures of (2)–(4) were repeated. Finally, the stretched specimen was fixed on a frame of board-paper and stored in a refrigerator.

### 2.2. X-ray diffraction measurement

Wide-angle X-ray diffraction apparatus employed was a R-Axis RAPID apparatus, RIGAKU, in the Department of Polymer Science and Engineering, Yamagata University. The machine outputs the diffraction intensity recorded on a cylindrical image-plate (radius = 127 mm, 460 mm (w) × 256 mm (h), 0.1 mm resolution) in a numerical format. For measurement, specimens were fixed on a frame with a 4 mm Ø hole, and mounted vertically on the machine’s goniometer and parallel to the meridian of image-plate.

### 2.3. X-ray data analysis

‘Windows’ programmes to evaluate the degree of

crystallinity, the degree of crystallite orientation and the size of crystallite were developed. Amongst, the procedure for the determination of the degree of crystallinity was as follows. At first, an data-array to store the intensity at an appropriate  $2\theta$  interval (i.e. 0.05°) is created for a  $2\theta$  range chosen (e.g. 10.00–40.00°). Then, in every data row (maximum: 2560), the pixel the  $2\theta$  of which is closest to a given value is sorted, and the intensity was accumulated in the array element. Thus, a randomised intensity curve is obtained. The air-scattering intensity measured separately and the incoherent scattering intensity calculated by conventional method are subtracted. As an amorphous reference, the unstretched rubber was employed. The degree of crystallinity was calculated as usual from the areas below the curves from crystalline and amorphous specimens.

The degree of crystallite orientation and the size of crystallite were obtained from the half-height width of azimuthal-scan curve and the half-height width of radial-scan curve, respectively.

The relationship between the geometry of cylindrical screen and a ‘virtual’ flat screens as well as the equations used for converting the coordinates is shown in Fig. 1.

### 2.4. Tensile test

Stress–strain measurement was conducted at 25 °C at the rate of ca. 4%/min with a laboratory-made tensile machine designed for enabling the measurement under controlled temperature, and assembled with a load-cell (Sensotec Model-34) and a rack-and-pinion linear motion unit (Oriental Motor 4LF10N4). A homemade computer

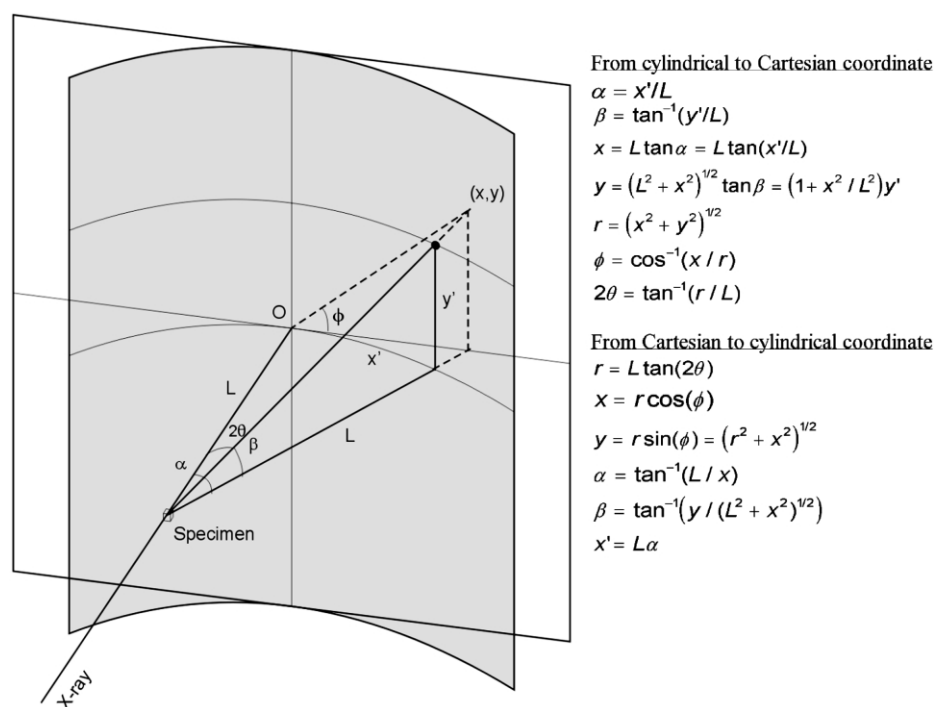


Fig. 1. Geometrical relationship between cylindrical and flat screens and equations for converting the coordinates.

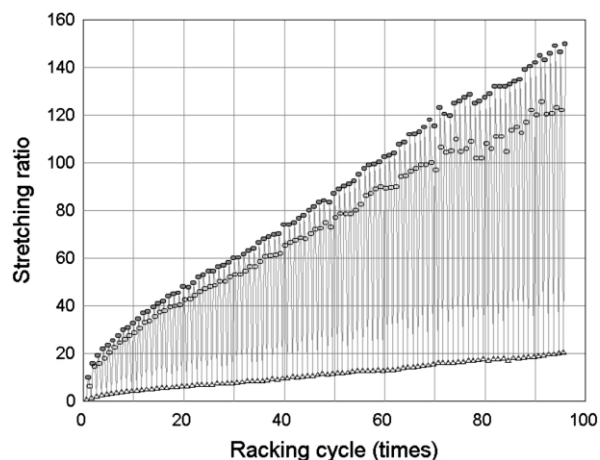


Fig. 2. Stretching ratio of smoked-sheet plotted vs repeated racking cycle. ● under tension, □ released at room temperature, △ relaxed at 75–85 °C.

programme was used to transfer and record the data via RS232 port. The Young's modulus was determined on another homemade programme in which the origin of the coordinate was correctable visually to optimise the fitting of initial slope to the stress–strain curve. For a technical reason, the stretched specimen had to be allowed to relax slightly for fixing on clamps. A small non-linear part thus observed in the initial part of stress–strain curve was ignored.

### 2.5. Theoretical calculation of crystal Young's modulus of natural rubber and its isomer

The calculation was carried out using the 'Cerius<sup>2</sup>' software installed by courtesy of Accelrys Inc. at the Department of Macromolecular Science, Osaka University, by inputting appropriate unit-cell constants and other parameters. The summary of calculation and the illustration of molecular conformation are shown in Appendix A.

### 2.6. Dissolution test and GPC measurement

Chloroform (40 ml) was added to a 0.2 g piece of stretched smoked-sheet and left overnight at room temperature. Undissolved fraction was collected by centrifuge to determine the gel content, whereas the supernatant solution was subjected to GPC measurement. The GPC machine used was composed of a Shimadzu LC-6A and other units for which an extra A/C converter was devised for transferring the data to computer via RS232C interface. The conversion of elution time to molecular weight, and the determination of average molecular weight were conducted on a homemade computer programme.

## 3. Results

Fig. 2 shows the change of stretching ratio vs racking. Although such a high stretch ratio as  $\times 150$  was attained by 96 cycles of racking in this run, it was experienced that the rubber specimens became weak and easy to break, and about 2–3 out of 10 specimens survived after some 60 cycles of racking, or  $\times 100$  of stretch ratio.

A set of wide-angle X-ray patterns of samples stretched up to various ratios, recorded on the image-plate, is shown in Fig. 3. Qualitatively, it is seen that the original unstretched rubber was amorphous and isotropic, and that oriented crystalline reflections appeared at such a low stretch ratio as  $\times 10$ , showing a typical fibre pattern.

Since no software suitable to analyse the fine structure of polymers was available, while all information necessary for the analysis is contained in the data, computer programmes to evaluate the degree of crystallinity, the degree of crystallite orientation and the size of crystallite were developed as described in Section 2. It has turned out that the degree of crystallinity reached the level of 17–18% at the stretch ratio of  $\times 20$  and tended to decrease after  $\times 60$ , as shown in Fig. 4. The degree of crystallite orientation evaluated in terms of half-height widths of azimuthal-scan curves for (200), (020), (201) and (021) reflections was as high as ca. 7.5° at  $\times 10$ , and stayed at the same level until the width tended to broaden slightly above  $\times 100$ , as shown in Fig. 5. The half-height widths of profiles, of radial-scan curves, of the same reflections determined as a measure of crystallite size were almost constant, being between 0.6 and 1.0°, and increased marginally after  $\times 100$ , as shown in Fig. 6.

Fig. 7 shows the results of tensile test. It was observed that the stress–strain relationships of stretched specimens were more or less linear, whereas the original smoked-sheet showed a typical trend of rubbery substance. The value of the Young's modulus increased with the stretch ratio and reached ca. 300 MPa at around  $\times 100$ , and thereafter decreased rather discontinuously, and the values scattered, as shown in Fig. 8.

## 4. Discussion

It is generally understood that the reason why the elongation of unvulcanised rubber under a load is limited at 6–8 times is due to the entanglement of molecular chains acting 'physically' like chemical cross-links [10]. That the 'natural draw ratio' observed in the cold-drawing of ordinary crystalline polymers does relate to the molecular entanglement has been made clear, after the discovery of gel-spinning method, or the dilute-solution-spinning method, with experimental data which fit the relationship, [maximum draw ratio] = [solution concentration]<sup>1/2</sup> [7,11].

Then, how the racking method could enable the elongation of natural rubber up to such a high stretch ratio

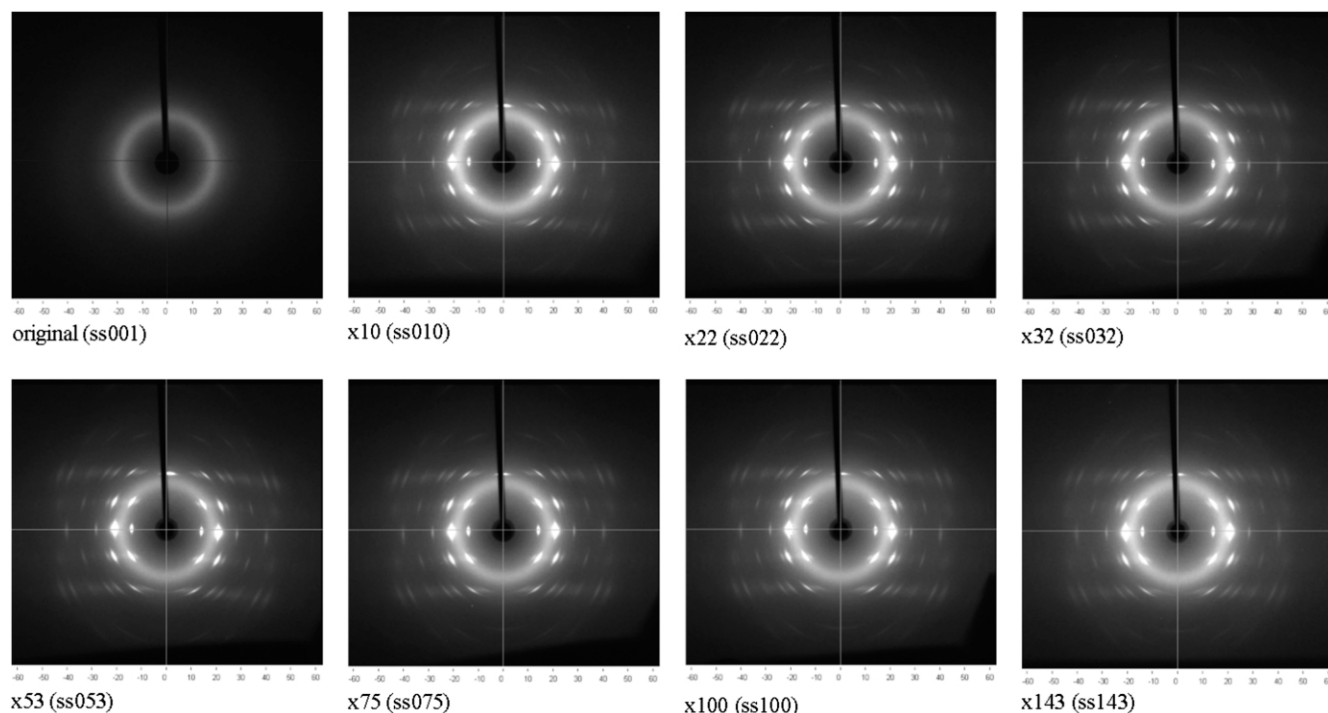


Fig. 3. Change of X-ray diffraction patterns of smoked-sheet by stretching.

as  $\times 150$ ? The question may be answered if one assumes that fractions of chain segments between entanglements, which had a broad distribution in their length, supposedly 'the most-probable distribution', were broken gradually in each step of stretching, rather than disentangled and slipped. Although the elongation was hindered in each step by the stress-induced crystallisation, further scission of chain molecules and accordingly elongation were enabled when the crystallised parts were re-melted and the molecular aggregation was re-randomised at high temperature. That the scission of chains could take place during the gel-drawing of polyethylene was discussed before [12]. The effect of chain scission on the structure and properties became apparent, when the number of effective chains that

could be extended and aligned parallel to the direction of the length would have decreased down below a certain level, as the degree of crystallinity and the Young's modulus turned to decrease after 30 and 60 times of racking, or  $\times 60$  and  $\times 100$  in stretch ratio, respectively.

As an auxiliary experiment, the solubility of specimens in chloroform was examined. The insoluble-fraction naturally contained in the raw natural rubber decreased with the stretch ratio, as shown in Fig. 9. This implies that the scission of entangled molecules had occurred, although no sensible change was observed for average molecular weight of dissolved fractions, the values of  $\bar{M}_n$  and  $\bar{M}_w$  being in the range of  $1.331 \pm 0.109 \times 10^6$  and  $2.270 \pm 0.180 \times 10^6$ , respectively.

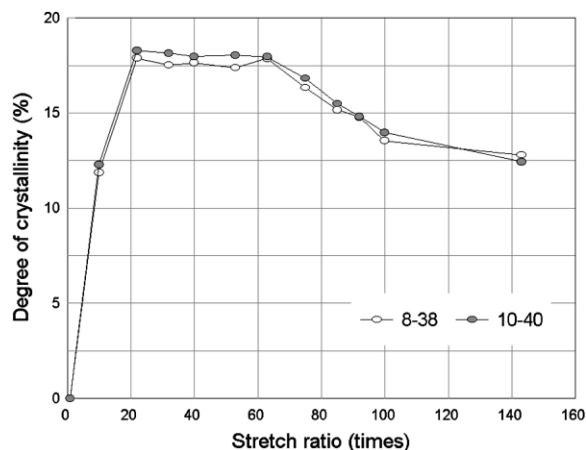


Fig. 4. The degree of crystallinity of smoked-sheet plotted vs stretch ratio (figures in the pane denote the  $2\theta$  range chosen for the evaluation).

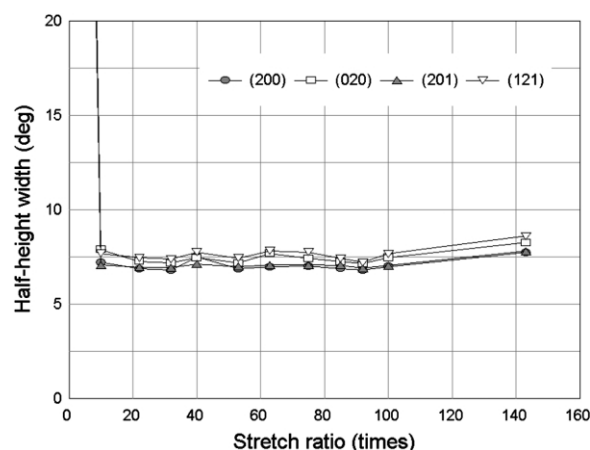


Fig. 5. Azimuthal-scan half-height width of reflections of smoked-sheet natural rubber plotted vs stretch ratio.

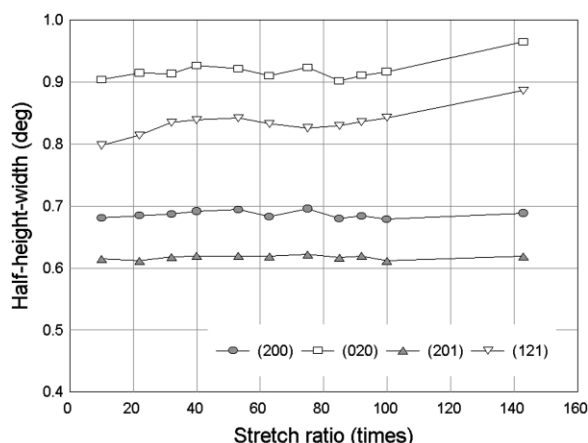


Fig. 6. Radial-scan half-height width of reflections of smoked-sheet natural rubber plotted vs stretch ratio.

Despite that the degree of crystallinity attained was as low as below 20%, the molecules which constituted crystalline parts were supposed to be well extended, bundled with each other, and highly oriented in the direction of the length, so as the stretched state is maintained at room temperature that is close to or higher than the melting temperature of poly-*cis*-isoprene. The value of melting temperature in literature ranges 14–36 °C [13].

The maximum value of Young's modulus attained, ca. 300 MPa, appeared to be very low compared to those of highly oriented fibres from other flexible polymers, e.g. >220 GPa, or ca. 70% of the theoretical value, for UHMWPE [14]. Since the theoretical Young's modulus of

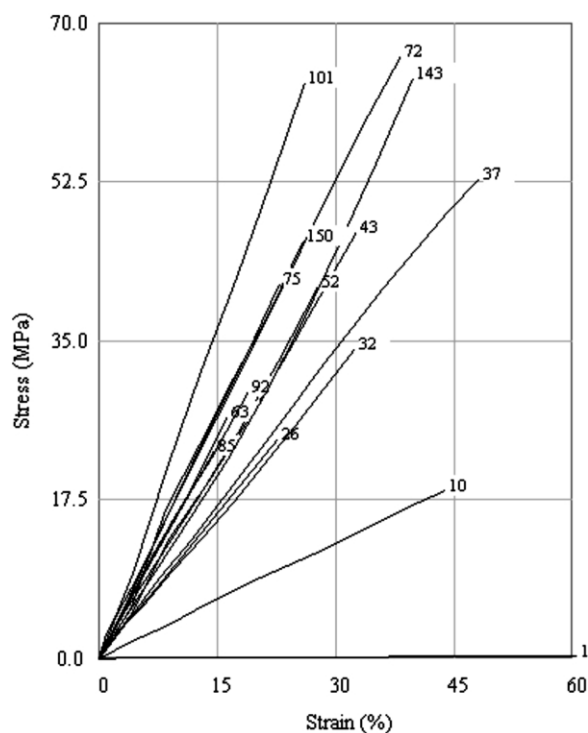


Fig. 7. Stress-strain curves of stretched smoked-sheet (computer output) (figures denote the stretch ratio).

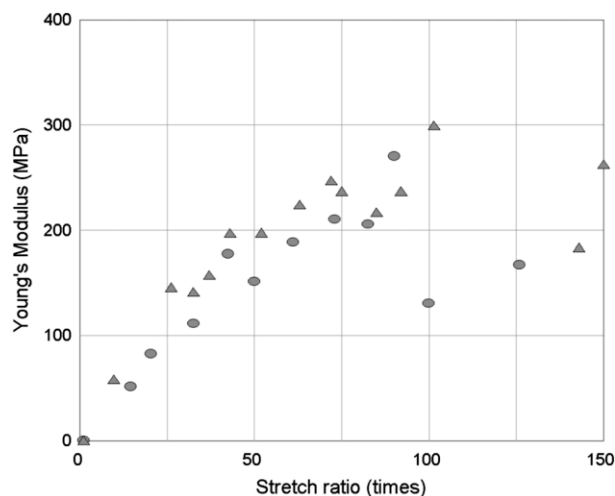


Fig. 8. The Young's modulus of stretched smoked-sheet plotted vs stretch ratio ● from the data of Fig. 6, Δ from another data set.

poly-*cis*-isoprene was not known to the authors, calculation was conducted and a value, 13.30 GPa was obtained (Appendix A). Comparing with this value, one may reckon that the Young's modulus of rubber attained by the racking method was just about 2% of the theoretical value, whilst the degree of crystallinity attained was 17–18%. This cannot be explained with a simple 'shish-kebab' type structural model, consisting of the core of extended molecules and epitaxially overgrown folded molecules, which has been depicted as the basic structure of slowly crystallised stretched rubber [5,15] as well as oriented fibres from crystalline polymers. The real structure of stretched rubber obtained by the racking method is considered to be more complicated, and more or less similar to the fringed micelle model, envisaged in the past for fibres, with irregular parts incorporated along the main core of extended and bundled molecules.

Above behaviour of smoked-sheet against the racking was similar with purified rubber obtained by Tanaka's method (enzyme decomposition of protein + ester exchange of chain-end groups [16]). In order to obtain a strong fibre by drawing technique, the control of molecular

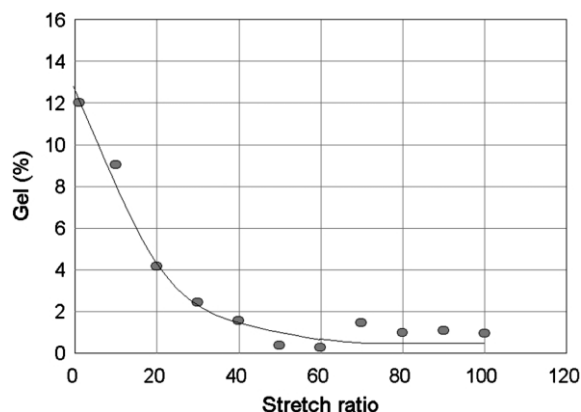


Fig. 9. Content of gel-fraction in smoked-sheet plotted vs stretch ratio.



Table A1  
Crystal Young's modulus and other mechanical constants

	Natural rubber	Gutta-percha ( $\alpha$ )	Gutta-percha ( $\beta$ )
Unit-cell parameters			
12.15	8.04	7.59	
$b$ (Å)	8.94	5.87	11.74
$c$ (Å)	8	8.85	4.7
$\alpha$ (degree)	90	90	90
$\beta$ (degree)	87.94	104.14	90
$\gamma$ (degree)	90	90	90
Density (g/cm <sup>3</sup> )	1.04	1.12	1.08
Bulk modulus (GPa)	8.54	10.55	9.37
Compressibility (GPa <sup>-1</sup> )	0.12	0.09	0.11
Young's modulus (Gpa)			
$x$	9.04	5.4	10.65
$y$	8.44	4.43	12.21
$z$	13.3	98.77	121.21
Poisson ratios			
$e_{xy}$	0.11	0.86	0.38
$e_{xz}$	0.35	-0.03	-0.02
$e_{yx}$	0.1	0.7	0.44
$e_{yz}$	0.36	0.04	0.05
$e_{zx}$	0.51	-0.46	-0.17
$e_{zy}$	0.57	0.87	0.5

Note: The three axes are defined as follows.  $z$ -axis: parallel to the chain axis;  $y$ -axis: set in the  $bc$  plane and perpendicularly to the  $z$ -axis;  $x$ -axis: perpendicular to the  $z$ - and  $y$ -axes.

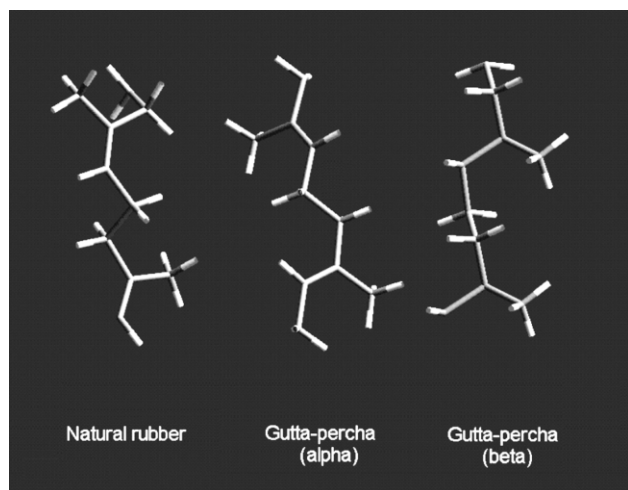


Fig. A1. Conformation of natural rubber and Gutta-percha.

entanglement is essential, besides the necessity to use a branchless linear polymer of very high molecular weight. Although natural rubber with  $\bar{M}_w > 2\,000\,000$  was regarded as a good candidate, attempt to prepare a xerogel by solution processing has been so far in vain.

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## Appendix A. Mechanical properties and conformation of natural rubber and gutta-percha (results of calculation)

Table A1 and Fig. A1.

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