ON THE STRETCHING OF CELLULOSE NITRATE FILM

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INTRODUCTION

It is one of the most important investigations in the field of high polymer that we make clear the relation between the properties and molecular structure of high polymer. We have many reports dealing with the relation. The fact that the properties of fibers are affected by the degree of orientation of the linear molecules in fibers has been made clear in the reports.

There are many methods that we use in order to orient the linear molecules in a given direction, and stretching in the softened state is one of the easiest methods for explaining the experimental data and is also the one that has been playing its great part, as is seen in the cold drawing of nylon, in the spinning process to increase the strength of fibers. Moreover, the stretching is a method by which we can conjecture the state of molecules not only in the swelling state of high polymer but also in the neighbourhood of its melting point.

Physical studies, such as the method of X-ray, on films or fibers whose degree of molecular orientation has been elevated by stretching are reported in many papers, but there is none that discusses the relation between stretching conditions and the properties of stretched films, and the change of molecular state in the softening process, excepting Funahashi's reports on synthetic high polymer films. In this paper, the changes of properties of cellulose nitrate films by stretching are explained and discussed. The reasons for using films as test pieces are as follows :

(1) Films can be made more easily than fibers or moulding pieces.

(2) It is convenient to measure the changes of properties in the directions other than stretching direction.

(3) The section area of a test piece can be regulated within suitable ranges.

(4) Many experiments can be made with a little sample.

(5) In the study of stretching it is necessary to use samples as isotropic as possible, and isotropic films can be obtained more easily than fibers.

EXPERIMENTAL METHOD

The films of cellulose nitrate (made at the Dainihon Celluloid Co., the content of nitrogen : 10.9%, the degree of polymerization : 225) were prepared by evaporating the $3\sim5\%$ acetone solution, from which floating material had been removed by filtration, on a glass plate placed on the surface of mercury in a desiccator, and were dried at a vaccum of $10\sim50$ mmHg at nearly 50°C for 6 hours.

The thickness of each film was calculated from the weight of its area $50\times50\text{mm}^2$ and its specific gravity measured by ups and downs method. The thickness was also measured under the microscope. It was recognized that the thickness of the former coincided with that of the latter.

The film was cut to test pieces of 1 mm in width on a section paper with a blade, and these pieces were on a paper frame in the cutting order as seen in Fig. 1 (A). The paper frame was cut into test pieces one by one, as seen in Fig. 1 (B), when measured or stretched. The error in the width of test pieces was nearly + 0.05 mm, but the error resulting from the width error could be controlled less than 1% by using ten or more pieces and by measuring these pieces one by one in the same order as cut off, so especially we did not correct the width by measuring under the microscope.

Test pieces of 10 mm in length were used in this experiment. Stretching was done in various swelling agents at a constant temperature by means of such a stretching apparatus as seen in Fig. 2.

In case the acetone-water system was adopted as a swelling agent, the films of cellulose nitrate could be stretched to a high degree in the swelling agents of the wide range of the rate from 1 : 4 to 4 : 1.

The stretching speed of about 1 mm/sec. was adopted as the standard, because it could be ascertained that a slight change of the speed had unexpectedly almost no

Paper Frame

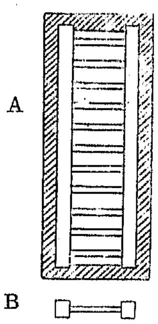

Fig. 1
Test piece

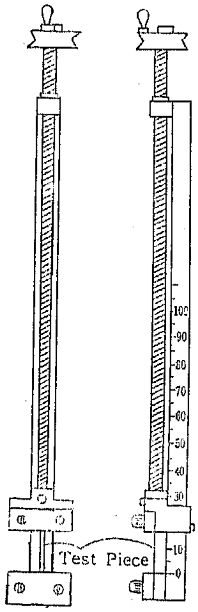

Fig. 2
Stretching apparatus

effect upon the properties of stretched films.

After stretching the films were dried in air fixed on the stretching apparatus. Tensile strength, elongation and Young's modulus of the stretched films were measured with the K-S type senimeter at 20°C, and their degree of double refraction was calculated from the thickness of the films and that retardation of the polarized light through the films which was measured with the Berek's compensator. The thickness of the stretched films was calculated on the assumption that stretching was done uniformly and did not change the specific gravity. In addition, the thickness of the films was measured directly under the microscope, and it was ascertained that both values of thickness agreed completely. The angle of inclination i was measured by Berek's compensator, and the retardation was obtained from Berek's table. Compensator constant c was 0.7576 according to Berek when the D-line of natrium lamp (589 mμ) was used at room temperature (20~25°C).

The degree of double refraction could be calculated from the following equation.

$$n_\gamma - n_\alpha = \frac{c\Gamma}{d}$$

$n_\gamma - n_\alpha$; degree of double refraction

d ; thickness of sample

The natrium lamp made at the Matsuda Company was used as the source of light in this experiment.

RESULTS

I. The Changes of Tensile Strength, Elongation and Young's Modulus caused by Stretching

1. In the Direction of Stretching

Table 1 shows the changes of various properties of cellulose nitrate films caused by stretching in swelling agents of various compositions. The tensile strength increased as a rule with the degree of stretching but there was the maximum point in the tensile strength-stretching degree curve in case of a swelling agent rich in solvent. For example, the tensile strength of films stretched in a swelling agent of acetone 5 : water 2 increased till 7 times stretching and decreased thereafter, with the degree of stretching. This is due to the high power of the swelling agent, i.e. from the fact that films became loose with increase of stretching degree it seemed that, in a high degree of stretching and at a stretching speed of 1 mm/sec., the orientation of molecules in a stretched film was overcome by the molecular

Table 1. The influence of stretching upon the mechanical properties of cellulose nitrate films stretched in various swelling agents at 25°C

Degree of stretching (Times)	Composition of Swelling Agents (Acetone : Water)								
	5 : 2			2 : 1			3 : 2		
	T. S.	E.	Y. M.	T. S.	E.	Y. M.	T. S.	E.	Y. M.
1	11.9	20.9	202	11.9	20.9	202	11.9	20.9	202
1.5	15.8	41.2	228	16.3	34.8	273	16.8	26.9	284
2	17.3	42.1	289	18.3	35.7	304	18.9	25.9	314
3	18.7	35.0	318	20.2	33.0	343	21.7	23.0	383
4	20.8	33.1	337	22.4	30.7	389	25.1	19.7	472
5	23.6	25.8	385	27.0	24.1	465	34.5	15.9	596
6	23.7	23.4	397	29.2	23.2	488			
7	24.1	16.1	476	33.3	20.4	505			
8	19.1	17.7	481	38.2	17.3	553			
9	18.9	16.8	470	41.8	14.4	648			
10	18.8	16.5	443	38.5	14.5	667			

Abbreviations T.S. Tensile strength Kg/mm^2 E. Elongation %
Y.M. Young's modulus Kg/mm^2

disturbance resulting from swelling. This result was also confirmed from the data of elongation and Young's modulus of the films. It was observed that the tensile strength of films stretched in a swelling agent rich in water was stronger than that stretched in an agent poor in water when compared at the same degree of stretching.

In the elongation-stretching degree curve, the writer could find the maximum point that is characteristic in case of stretching of high molecular compound films. Fig. 3 shows the changes of elongation of various cellulose derivative films by stretching. The maximum point in the elongation-stretching degree curve is apparently found all in case of cellulose acetate, benzylcellulose and ethylcellulose. This interesting fact was found at first in the stretched films of polyvinylchloride and polymethylmetacrylate by Dr. Sakurada, and later Funahashi found it in the films of various synthetic high compounds.

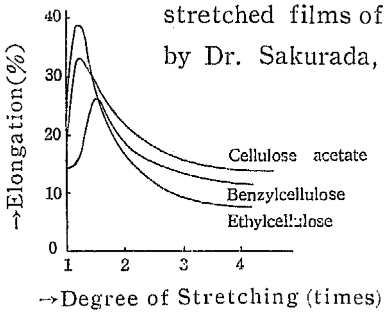

Fig. 3

The writer found it also in the films of various cellulose derivatives (15). According to Table 1, the maximum point was higher in films stretched in an agent rich in acetone than in those in an agent poor in acetone, and the position of maximum point seemed to move slightly to the high degree of stretching as the swelling agent became richer in acetone. When compared at the same degree of stretching, the elongation of films stretched in an agent rich in acetone was higher than those in an agent poor in acetone. Moreover, when stretched in a swelling agent of acetone 5 : water 2, the elongation of 7 times-stretched films showed the minimum value. This can be explained from the high power of the swelling agent as in case of the tensile strength.

The change of Young's modulus of films by stretching showed entirely the same tendency with that of those tensile strength.

The changes of the properties of cellulose acetate films stretched in dry heated air showed the same inclination with those of cellulose nitrate films stretched in swelling agents, and the composition of agents in case of swelling stretching was equivalent to the temperature in case of stretching in dry heated air.

The following is a description about cellulose nitrate films containing plasticizer, i. e. camphor 20 % or 30 %. Table 2, Table 3 show the changes of various properties of cellulose nitrate films containing camphor by stretching in various swelling agents. In case of non-stretched cellulose nitrate films containing camphor, tensile strength and Young's modulus decreased with increase in camphor content and elongation increased with the film containing 20 % camphor and decreased with that of 30% camphor. In the

Table 2. The influence of stretching in various agents upon the mechanical properties of cellulose nitrate films containing camphor 20%

Degree of Stretching (Times)	Composition of swelling Agents (Acetone : Water)								
	5 : 2			2 : 1			3 : 2		
	T. S.	E.	Y.M.	T. S.	E.	Y.M.	T. S.	E.	Y.M.
1	9.8	22.1	195	9.8	22.1	195	9.8	22.1	195
1.5	10.2	47.2	192	15.1	32.7	235	17.3	31.9	268
2	11.9	40.6	203	18.0	33.6	288	25.3	27.1	342
3	14.3	39.0	229	21.2	31.6	325	28.7	21.0	423
4	18.0	37.8	246	24.5	30.2	366	29.5	17.9	441
5	20.2	36.1	311	28.3	29.4	398			
6	22.3	35.4	358	31.0	27.2	446			
7	26.4	35.2	445	31.7	25.2	481			
8	23.7	32.3	442	29.8	23.1	513			
9	23.2	29.8	434						
10	23.2	28.5	437						

Table 3. The influence of stretching in various agents upon the mechanical properties of cellulose nitrate films containing camphor 30%

Degree of Stretching (Times)	Composition of Swelling Agents (Acetone : Water)								
	5 : 2			2 : 1			3 : 2		
	T. S.	E.	Y.M.	T. S.	E.	Y.M.	T. S.	E.	Y.M.
1	7.2	19.9	148	7.2	19.9	148	7.2	19.9	148
1.5	7.9	31.3	142	10.3	27.3	178	11.3	23.2	211
2	9.0	35.4	157	12.8	29.1	195	14.5	23.1	256
3	10.7	34.5	181	15.7	26.9	252	17.4	19.9	303
4	13.2	32.3	206	19.7	24.4	302	20.9	15.6	369
5	14.9	31.9	225	23.1	21.7	365			
6	15.7	30.5	265	25.5	20.1	403			
7	17.2	26.1	314	25.3	18.7	456			
8	17.2	25.1	321	25.9	17.4	489			
9	17.1	23.3	322						
10	17.0	22.5	313						

previous experiment the tensile strength and elongation of cellulose acetate films increased with plasticizer content but the plasticizer content in this case was low, i.e. up to 5%.

In films containing camphor, 10 times stretching was very easy in a swelling agent of acetone 5 : water 2, and 8 times stretching was possible in an agent of acetone 2 : water 1, and only 4 times stretching was possible in acetone 3 : water 2. That is to say, the highest possible stretching degree became low by containing plasticizer not only in this case but also in the case of cellulose acetate. Generally, the effect of stretching upon the tensile strength and Young's modulus of cellulose nitrate films showed the same tendency with the case of other cellulose derivative films.

The effect of plasticizer containing upon stretching efficiency was as follows, viz., tensile strength of cellulose nitrate films containing 20% camphor showed the greatest percentage of increase in strength regardless of any composition of swelling agents, and the highest strength in this case was higher than that of no camphor films in an agent of acetone 5 : water 2. The tensile strength of cellulose nitrate films containing 30% camphor showed the lowest value when compared not only at the same stretching degree but also at the highest strength, and the rate of increase in strength by stretching in this case was a little higher than that of no camphor films, and in an agent of acetone 5 : water 2 the rate of decrease in strength in the stretching degree over 8 times was the least when compared with films containing no camphor and 20% camphor.

Next, in case of films in which the same amount of camphor was contained, the effect of swelling agents upon tensile strength was as follows; tensile strength at the same degree of stretching was greater and the rate of increase in strength by stretching was higher in case of stretching in a swelling agent rich in non-solvent than in case of one rich in solvent. The highest tensile strength in the films in which camphor content was the same, was obtained in case of stretching in a swelling agent of acetone 2 : water 1. Therefore it could be understood that the swelling agent of acetone 5 : water 2 had too high swelling-power for and the agent of acetone 3 : water 2 had too low power for stretching.

Regarding elongation, in cellulose acetate films the maximum value in the elongation-stretching degree curve became eminent by containing plasticizer, but in cellulose nitrate films the maximum value was almost unchanged by containing plasticizer. This fact showed that the swelling agent of acetone-water system had very large swelling-power toward cellulose nitrate films, consequently made it possible to stretch smoothly even if plasticizer was not contained in it. The decrease of elongation after maximum point which was caused by the increase of stretching degree was lessened by camphor containing, and even the elongation of camphor containing films 10 times stretched in a swelling agent of acetone 5: water 2 was higher than that of non-stretched films. When films containing the same amount of camphor were compared at the same degree of stretching, the elongation of films stretched in a swelling agent rich in solvent was higher than that in an agent poor in solvent, and also the rate of decrease after maximum point in the former was less than that in the latter.

Under the same degree of stretching, the more camphor was contained in films or the richer in solvent a swelling agent was, the less the Young's modulus of films stretched was.

2. At various Angles to the Direction of Stretching

It was observed generally in the stretching of high polymer films that the tensile strength and Young's modulus in the stretching direction increased with stretching degree and the maximum point was found in the elongation-stretching degree curve. It is well known that if micells or molecules in fibers are orientated too well, fibers from cellulose become so stiff like wire and so brittle as to be worthless. H. Lohmann (1) concluded in his report on the stretching of cellulose acetate fibers in a swelling agent, that when the degree of molecular orientation was high, the tensile strength was remarkably high, but the elongation or bending strength was so low that the fiber was brittle.

Table 4 shows the result of cellulose nitrate films stretched in a swelling agent of acetone 2 : water 1. In this case films of 50×50 mm square were used as samples. When wide films were stretched, they shrinked remarkably in the direction of width and the change of their area was little before and after stretching. As both end of a film was fixed on the stretching apparutus, it was stretched like a concave lens.

Table 4. The changes of mechanical properties of cellulose nitrate films in various directions by stretching in acetone 2 : water 1

Stretching Degree (Times)	at the Direction of Stretching		at Right Angles to the Direction of Stretching		at 45°to the Direction of Stretching	
	T. S.	E.	T. S.	E.	T. S.	E.
0	11.9	20.9	11.9	20.9	11.9	20.9
1.5	17.5	34.4	10.6	16.3	13.3	24.6
2	19.2	34.8	6.1	8.7	8.8	13.8

According to Table 4, both tensile strength and elongation at right angles to the stretching direction decreased remarkably and could not be measured with films stretched over 2 times, because the films were very brittle. And it was also very difficult to stretch films over 2 times of stretching degree. According to the previous data, the elongation of cellulose nitrate films in the direction of stretching increased remarkably in such a low degree of stretching, but the elongation at right angles to the direction of stretching decreased remarkably by stretching. The tensile strength and elongation at 45° angles to the direction of stretching showed intermediate values between those in the direction of stretching and those at right angles to it, and had the maximum value at 1.5 times degree of stretching.

As described above, films were stretched like a concave lens, so the reappearance of the results was unsatisfactory. Then the experiment was stopped here.

3. The Effect of Stretching Speed

When films are stretched in swelling agent, linear molecules in the films are orientated to the direction of stretching and the swelling agent is pressed out. On the other hand, the orientation of molecules is disturbed owing to the diffusion and osmosis of swelling agent into the films. Therefore stretching speed will have a considerable effect upon the properties of the stretched films. In brief the higher the stretching speed, the greater the efficiency of stretching is, so far as the film do not break. But it is not so simple in practice, and it seems that the strain of molecular orientation in stretching comes to a stable state during the delay of time, so there exists a stretching speed most suitable for a stretching condition.

The effects of stretching speed on the properties of stretched films were examined, and they are shown in Table 5. These effects were unexpectedly very small, excepting the case of extremely high or low stretching speed, i. e. in the neighbourhood of 1 mm/sec..

Table 5. Effects of stretching speed on the mechanical properties of the stretched films of cellulose nitrate (3 times stretched film)

Stretching Speed (mm/sec)	Composition of Swelling Agents (Acetone : Water)					
	5 : 2			2 : 1		
	T. S.	E.	Y.M.	T. S.	E.	Y.M.
5	19.2	30.4	336	19.6	26.8	324
1	18.7	35.0	318	20.2	33.0	343
0.2	17.2	40.6	302	19.5	35.4	325
0.05	13.5	37.9	243	18.1	38.6	308

II. The Effect of the Polymerization Degree of Cellulose Nitrate on various Properties.

1. Fractionation of Cellulose Nitrate

Fractionation of cellulose nitrate has been frequently investigated. Early work was done by W. Kumichel (2), K.Werner and H. Engelman (3), J. Clark and F. D. Niles (4), E. Ber land O. Hefter (5), J. Duclaux and J. Barbiere (6) and A. J. Medvedev (7). Thereafter this question was more thoroughly studied by J. W. Mcbain and D. A. Scott (8), H. M. Spurlin (9) and H. Dolmetsch and F. Reinecke (10). Moreover, when the distribution of polymerization degree of cellulose was measured, fractionation was done usually after changing cellulose into cellulose nitrate, so fractionation work from this field was done by many investigators such as Schieber (11) and O. Eisenhut (12).

In this work fractionation was done by fractional precipitation making reference to the method of P. C. Scherer and Li-Hsi Lou (13). Namely, cellulose nitrate was fractionated into 4 parts by adding a precipitant of water 3 : acetone 2 to the 3.5% solution in which cellulose nitrate was dissolved in a mixed solvent of acetone 3 : ethyl acetate 7. Moreover each of the parts was fractionated into 3 parts with the same procedure. Table 7 presents the most suitable condition for fractionation under various contents of nitrogen in cellulose nitrate, as given by P. C. Scherer.

Table 6. Various properties of fractionated cellulose nitrate

No. of Sample	Yield (%)	Intrinsic Viscosity $[\eta]$ (100ml/g)	Degree of Polymerization	Tensile Strength (kg/mm²)	Elongation (%)	Young's Modulus (kg/mm²)
Original	100	2.25	225	11.9	20.9	202
Fr.1 No.2	4.37	3.40	340	15.4	22.3	271
Fr.2 No.1	13.09	2.34	234	13.6	21.0	252
Fr.3 No.2	7.84	1.45	145	11.2	18.6	192
Fr.4 No.1	6.87	1.12	112	10.3	16.5	188
Fr.4 No.3	6.05	0.56	56	7.7	11.7	180

$Km = 10 \times 10^{-4}$

Table 7. The most suitable condition for fractionation under various contents of nitrogen in cellulose nitrate

Nitrogen content (%)	Concentration (%)	Solvent		Precipitant	
		Ethylacetate (%)	Acetone (%)	Water (%)	Acetone (%)
10.97	3.5	30	70	60	40
12.10	2.5	20	80	60	40
12.55	2.5	20	80	75	25
13.55	2.5	20	80	75	25

The results of the fractionation are recorded in Table 6. The results of viscosity measurements in cellulose nitrate conformed quite closely to Baker-Philippoff's equation, so intrinsic viscosity, $[\eta]$, was calculated from the following equation.

$$[\eta] = \frac{8}{c}\left(\eta_r^{\frac{1}{8}} - 1\right)$$

where η_r = relative viscosity

According to Staudinger's rule, the polymerization degree, P, of a linear high polymer is related to its intrinsic viscosity by the expression:

$$[\eta] = K_m P$$

where K_m = Staudinger's constant

Table 8 presents the relation of K_m and the nitrogen content, as given by Wannow (14) and Scherer and Lou (13). The nitrogen content of cellulose nitrate treated in this work was 10.9 %, so polymerization degree was calculated by using $K_m = 10 \times 10$. Table 6 shows that the tensile strength, elongation and Young's modulus increase with the polymerization degree.

Table 8. Staudinger's constant as function of nitrogen content

Wannow		Scherer and Lou	
Nitrogen Content(%)	Km	Nitrogen Content(%)	Km
10.70	9.7×10^{-4}	10.97	10×10^{-4}
12.11	11.6	12.10	11.6
12.75	13.0	12.12	11.6
13.60	17.4	12.55	12.5
13.79	17.7	13.35	16.8

The relation of polymerization degree to tensile strength, F, can be expressed by the following equation and the relation of F·P to P shows a straight line as seen in Fig. 4.

$$F = A - \frac{B}{P}$$

where A or B = a constant

It was a surprise that even the cellulose nitrate film of extremely low polymerization degree such as 56 could be formed and had mechanical strength, though small. This film could not be obtained, however, unless it was treated carefully. Cellulose nitrate films could be formed in lower polymerization degree than cellulose acetate films.

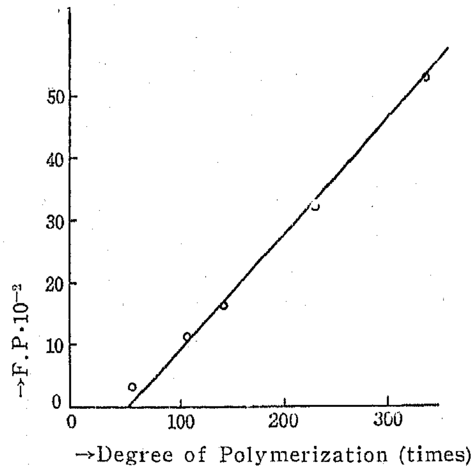

Fig. 4

2. **Stretching in Swelling Agents**

Each film of the five fractions presented in Table 6 was stretched 1.5~10 times in a swelling agent of acetone 2: water 1 at 25°C. The measurements of the properties are shown in Table 9. The properties of non-stretched films are shown also in Table 9 for reference. It was found that the difficulty of stretching procedure was due to the difference of polymerization degree. According to Table 9, possible stretching degree becomes low with increase in polymerization degree. But even 1.2 times stretching could not be done in the fraction of extremely low polymerization degree such as P=56. It seemed to be caused by the low power of the swelling agent that only films of low stretching degree were obtained in the fraction of high polymerization degree. There seemed to be an agent of composition suitable for each polymerization degree.

Table 9. The changes of various properties of fractionated cellulose nitrate films caused by stretching

(Stretching in a sewlling agent of acetone 2 : water 1)

Degree of stretching (Times)	Original			P=340			P=234		
	T. S.	E.	Y.M.	T. S.	E.	Y.M.	T. S.	E.	Y.M.
1	11.9	20.9	202	15.4	22.3	271	13.6	21.0	252
1.5	16.3	34.9	273	23.0	23.8	413	16.6	35.7	307
2	18.3	35.7	304	28.2	20.4	486	21.1	38.8	371
3	20.2	33.0	343				24.7	35.4	415
4	22.4	30.7	389				28.2	31.8	496
5	27.0	24.1	465				30.2	29.6	523
6	29.2	23.2	488				35.1	25.3	578
7	33.3	20.4	505				39.8	22.6	626
8	38.2	17.3	553				42.1	17.6	690
9	41.8	14.4	648						
10	38.5	14.5	667						

Degree of Stretching (Times)	P=145			P=112			P=56		
	T. S.	E.	Y.M.	T. S.	E.	Y.M.	T. S.	E.	Y.M.
1	11.2	18.6	192	10.3	16.5	188	7.7	11.7	180
1.5	16.4	37.2	257	13.7	37.1	264			
2	17.3	36.5	304	14.4	32.9	285			
3	21.9	34.2	348	15.7	31.9	313			
4	23.2	33.3	376	18.8	30.8	356			
5	28.0	30.4	435	18.9	28.2	391			
6	31.0	27.2	473	18.8	23.8	429			
7	32.5	25.1	497	18.6	22.9	456			
8	34.8	22.4	546	17.7	20.6	520			
9	36.7	17.5	607	17.0	19.4	537			
10	36.5	17.4	633	16.2	19.0	542			

The tensile strength increased generally with stretching degree, but in the fraction of low polymerization degree such as P=111, the film stretched 5 times showed the maximum value of tensile strength and thereafter the strength decreased with stretching degree. It seemed that the power of a swelling agent of acetone 2 : water 1 was too large for the fraction of low polymerization degree. Within the limit of polymerization degree treated in this study, the higher the polymerization degree, the higher the tensile strength became under the same degree of stretching and besides the larger the rate of increase in strength with stretching degree became. In the case of cellulose acetate, the tensile strength of non-stretched or stretched films became remarkably strong through the uniform distribution or polymerization degree caused by fractionation, but in the case of cellulose nitrate this was not so remarkable although it was slightly perceived in the table.

The maximum point in the elongation-stretching degree curve could be found at the stretching degree of 1.5～2 times regardless of polymerization degree. It was an evidence of insufficient swelling in stretching procedure that the maximum point in the fraction P=340 was very low.

The Young's modulus increased nearly straight with stretching degree. In addition the higher the polymerization degree, the larger the Young's modulus became under the same degree of stretching.

As stated above, the films of the fraction P=340 could be stretched only two times in a swelling agent of acetone 2 : water 1. This fact was due to that low power of the swelling agent which was caused by insufficient acetone content. Then, when acetone content in a swelling agent increased higher and higher, i.e. when the rate of acetone to water changed from (2 : 1) to (5 : 2) and then to (3 : 1) and finally to (4 : 1), how did the properties of films of P=340 change ? Table 10 shows these results. The more the rate of acetone in a swelling agent, the higher the highest possible stretching degree became, and in an agent of acetone 4 : water 1 even 10 times stretching was easily possible. In addition, it was confirmed that any difference in nitrogen content between the fractions could not be found regardless of the difference in the swelling power.

Table 10. The mechanical properties of fractionated cellulose nitrate films in various swelling agents (P=340)

Degree of stretching (Times)	Composition of Swelling Agents (Acetone : Water)											
	2 : 1			5 : 2			3 : 1			4 : 1		
	T. S.	E.	Y.M.	T. S.	E.	Y.M.	T. S.	E.	Y.M.	T. S.	E.	Y.M.
1	15.4	22.3	271	15.4	22.3	271	15.4	22.3	271	15.4	22.3	271
1.5	23.0	23.8	413	22.3	30.2	397	20.6	32.7	369	18.3	34.0	329
2	28.2	20.4	486	25.3	30.7	464	22.2	34.1	445	20.9	36.2	394
3				33.4	23.9	603	25.1	34.0	538	22.7	40.3	456
4				36.9	18.8	672	28.9	30.3	621	24.6	35.7	496
5							33.3	27.2	697	28.2	31.4	558
6							40.2	20.5	744	35.8	27.5	609
7							45.5	17.2	818	35.4	25.3	637
8										34.7	21.1	685
9										33.5	19.2	722
10										29.5	18.9	763

The tensile strength increased generally with stretching degree, but in an agent of acetone 4 : water 1, the maximum point was found in the tensile strength-stretching degree curve. This was due to the fact that the swelling power of the agent was too large for the films of P=340. Under the same stretching degree, the less the rate of acetone in a swelling agent, the larger the tensile strength became, and the highest tensile strength was 45.5 kg/mm² in the film stretched 7 times in an agent of acetone 3 : water 1.

In the elongation-stretching degree curve, the maximum point was found also in this case, and the more the rate of acetone in a swelling agent, the higher the maximum value became. Under the same stretching degree the more the rate of acetone in an agent the higher the elongation became. Moreover the position of the maximum point shifted toward the high stretching degree with increase in acetone content in swelling agents. Namely the larger the swelling power, the higher the elongation became.

In all cases, the Young's modulus increased almost straight with stretching degree.

Ⅲ. The Changes of Double Refraction by Stretching

Table 11 shows the measurements of double refraction of cellulose nitrate films in case of stretching in a swelling agent of acetone 5 : water 2. According to the table, the double refraction of cellulose nitrate films shows positive value regardless of containing camphor.

Table 11. The double refraction of cellulose nitrate films stretched in various swelling agents

(A) Stretching in acetone : water=5 : 2

Degree of Stretching	1	1.5	2	3	4	5	6	7	8	9	10
$n_\gamma - n_\alpha$	0.000	0.0047	0.0057	0.007	0.0081	0.009	0.0094	0.0096	0.0084	0.0082	0.0081
Tensile Strength	11.9	15.8	17.3	18.7	20.8	23.6	23.7	24.1	19.1	18.9	18.8

(B) Stretching in acetone : water=2 : 1

Degree of Stretching	1	1.5	2	3	4	5	6	7	8	9	10
$n_\gamma - n_\alpha$	0.000	0.0048	0.0059	0.0077	0.0090	0.0105	0.0116	0.0134	0.0149	0.0161	0.0157
Tensile Strength	11.9	16.3	18.3	20.2	22.4	27.0	29.2	33.3	38.2	41.8	38.5

(C) Stretching in acetone : water=3 : 2

Degree of Stretching	1	1.5	2	3	4	5
$n_\gamma - n_\alpha$	0.000	0.0051	0.0071	0.0086	0.0102	0.0128
Tensile Strength	11.9	16.8	18.9	21.7	25.1	34.5

C=0.7675

The double refraction increased with stretching degree and was in parallel with the tensile strength. From the table, it was understood that the orientation of moleclues or micells in the film was disturbed by the high power of a swelling agent at a high stretching degree. Fig. 5

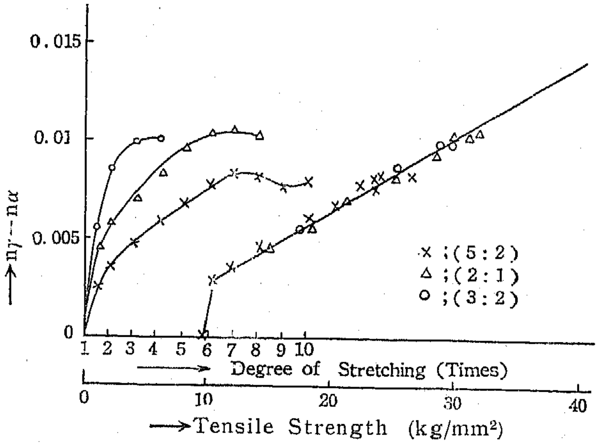

Fig. 5

shows the relation between the tensile strength and the double refraction of cellulose nitrate films, containing 20 % camphor, which were stretched in various swelling agents. The relation is shown with the same two straight lines regardless of the composition of swelling agents, This fact is very interesting. Under the same double refraction, the more the camphor content, the less the tensile strength became.

Next, Table 12 shows the double refraction of fractionated cellulose nitrate films stretched in a swelling agent of acetone 2 : water 1 at 25°C. Under the same polymerization degree, the higher the polymerization degree, the larger the double refraction became. Fig. 6 shows the relation

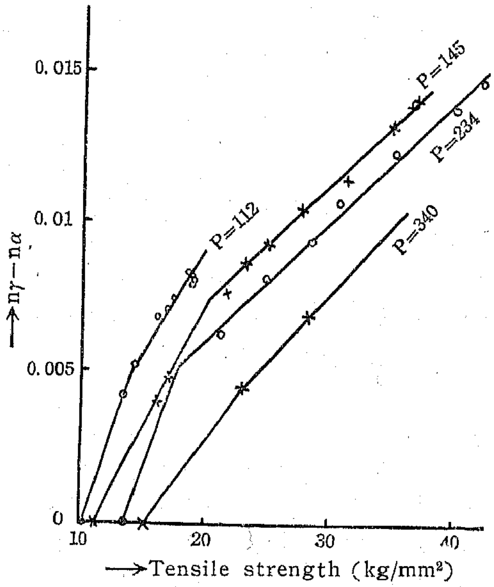

Fig. 6

between the tensile strength and the double refraction of fractionated cellulose nitrate films. The measurements about each film of

Table 12. The double refraction of fractionated cellulose nitrate films stretched in acetone 2 : water 1

P=340

Degree of Stretching	1	1.5	2
$n_\gamma - n_\alpha$	0.000	0.0045	0.0069
T.S.	15.4	23.0	28.2

P=234

Degree of Stretching	1	1.5	2	3	4	5	6	7	8
$n_\gamma - n_\alpha$	0.000	0.0036	0.0063	0.0081	0.0094	0.0108	0.0124	0.0139	0.0149
T.S.	13.6	16.6	21.1	24.7	28.2	30.2	35.1	39.8	42.1

P=145

Degree of Stretching	1	1.5	2	3	4	5	6	7	8	9	10
$n_\gamma - n_\alpha$	0.000	0.0039	0.0048	0.0076	0.0087	0.0104	0.0115	0.0124	0.0133	0.0142	0.0140
T.S.	11.2	16.4	17.3	21.9	23.2	28.0	31.0	32.5	34.8	36.7	36.5

P=112

Degree of Stretching	1	1.5	2	3	4	5	6	7	8	9	10
$n_\gamma - n_\alpha$	0.000	0.0042	0.0053	0.0061	0.0079	0.0081	0.0083	0.0084	0.0075	0.0071	0.0069
T.S.	10.3	13.7	14.4	15.7	18.8	18.9	18.8	18.6	17.7	17.0	16.0

C=0.7675

different polymerization degree were placed on two straight lines. Moreover under the same strength the lower the polymerization degree, the greater the double refraction became, namely in case of the same orientation of moleclues the tensile strength of the film of low polymerization degree was higher than that of high polymerization degree.

SUMMARY

This paper dealt with the stretching studies of cellulose nitrate films, plasticizer containing cellulose nitrate films and fractionated cellulose nitrate films. That is to say, the changes in the various properties of these films by stretching in swelling agents were investigated, and the following results were obtained.

1. The tensile strength and Young's modulus in the direction of stre-

tching increased generally with the stretching degree. But in case of stretching in a swelling agent rich in solvent, the maximum point was found in the tensile strength-stretching degree curve, and this fact was due to the high power of the swelling agent.

2. Regarding the elongation in the direction of stretching, the maximum point was found in the elongation-stretching degree curve, and the maximum value was almost unchanged by containing plasticizer. The maximum point was higher in films stretched in a swelling agent rich in acetone than in those in an agent poor in acetone.

3. The mechanical properties of the films at right angles to the direction of stretching were degraded remarkably by stretching, and those at 45° angles to the direction of stretching showed intermediate values between those at the direction of stretching and those at right angles to it.

4. The effects of stretching speed on the mechanical properties were unexpectedly very small except in the case of extremely high or low stretching speed.

5. Even the fraction of extremely low polymerization degree such as 56 had ability of film formation, and the film produced in this way had small mechanical strength though brittle.

The relation of polymerization degree to tensile strength in non-stretched films could be expressed by the following equation:

$$F=A-\frac{B}{P}$$

The efficiency of stretching increased slightly by the uniform distribution of polymerization degree caused by fractionation.

The highest tensile strength 45.5 Kg/mm^2 was obtained in that film of the fraction P=340 which was stretched 7 times in an agent of acetone 3 : water 1.

6. Regarding the double refraction, it was in parallel with the tensile strength, and the higher the stretching degree, the larger the double refraction became. The relation of tensile strength to double refraction of cellulose nitrate was shown by the same two straight lines regardless of the composition of swelling agents so far as the same sample was used. In case of the same orientation of molecules, the tensile strength of the film of low polymerization degree was higher than that of high polymerization degree.

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