ON THE STRETCHING OF CELLULOSE DERIVATIVE FILM

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INTRODUCTION

High polymeric substances are put to practical use widely in every field because of their excellent properties, and we are now in the days of high polymer. 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.

There are two factors by which the properties of high polymer are influenced: one is the effect of the chemical structure, chain length, and shape of high polymer molecules on the properties, and the other is that of the aggregating state of high polymer molecules on the properties.

Table 1. Connection between Properties and Structural Characteristics of High Polymers

Property	Average Polymerization Degree	Branching	Cross Linking	Homopolar Nature	Heteropolar Groups	Flexibility of Chains	Readiness of Chains to Crystallize	Orientation of Crystallites
Modulus of Elasticity	+	?	+	?	?	−	+	+
Ultimate Tensile Strength	+	?	?	−	+	?	+	+
Ultimate Impact Strength	+	?	−	+	?	+	−	−
Elongation to Break	+	?	−	+	?	+	−	−
Range of Elastic Extensibility	+	−	−	+	?	+	?	?
Tendency to Contract	+	?	−	+	−	+	−	?
Surface Hardness	+	?	+	−	+	−	+	+
Resistance to Temperature	+	?	+	−	+	−	+	?
Electric Resistance	?	?	+	+	−	?	?	?
Dielectric Constant	?	?	?	−	+	?	?	?
Resistance to Swelling	+	+	+	?	?	−	+	+
Resistance to Moisture	+	+	+	?	?	−	+	+
Resistance to Acids and Alkalies	?	?	+	+	?	?	+	?
Adhesive Power	?	+	−	?	+	+	−	−

A plus sign means that the structural feature increases the property under consideration; a minus sign means that it decreases it,

Table 1. gives an approximate picture[1] of the above-mentioned situation, showing the connection between some properties of high polymer and structural characteristics such as orientation of crystallites, average polymerization degree, heteropolar groups, cross linking etc.

Studies[2][3][4][5][6] on the stretching of various cellulose derivative films have been made systematically in our laboratory, with the intention of making clear the relation between the mechanical properties and molecular structure of high polymer, and moreover with a view of practical use.

There are many methods that we can use in order to orientate 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 played its important part, as is seen in the cold drawing of nylon and the other synthetic fibers. The phenomenon of cold drawing observed on polymeric substances is important in the manufacture of synthetic fibers, e. g. polyamide, polyester, after-chlorinated-polyvinylchloride etc., because their mechanical properties are remarkably improved by stretching.

The results obtained from the experiment of stretching of cellulose derivative films are summarized in this paper, and the stretching mechanism is discussed on these results. The method of the experiment is, of course, one of the indirect measurements in explaining the stretching mechanism, so we can obtain only qualitative results about the stretching mechanism without reaching any conclusion. The reasons for using films as test pieces are stated in the preceding paper.[6]

EXPERIMENTAL METHOD

Each film of cellulose derivatives was prepared by evaporating, on a glass plate on the surface of mercury in a desiccator, each of those 3~5% volatile solvent solutions from which floating material had been removed by filtration, and was dried in a vacuum evaporator at a vacuum of 10~50 mmHg at nearly 50°C for 6 hours.

The thickness of each film was calculated from the weight for its unit area and its specific gravity measured by the ups and downs method. The thickness was also measured under the microscope and the thickness measured by the former coincided with that by 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 pasted on a paper frame in the cutting order. The paper frame was cut one by one into test pieces when measured or stretched.

The cellulose derivatives used in this experiment were cellulose acetate,[2,4] cellulose acetate containing plasticizer,[2] ethylcellulose,[3] benzylcellulose,[3] cellulose nitrate,[6] cellulose nitrate containing camphor,[6] carboxymethylellulose,[5] saponified cellulose acetate,[4] and cellulose xanthate.[5] In the case of cellulose xanthate the sample was made by natural flowing, so the test pieces were not in the form of films but filaments.

Stretching was done in various swelling agents at a constant temperature or in the softened state in dry heated air at a constant temperature, with a stretching apparatus.[6] The swelling agent consisted of a definite percentage mixture of solvent and nonsolvent. The stretching speed of about 1 mm/sec. was adopted as the standard, because it could be ascertained that a slight change in the speed unexpectedly had almost no effect[5] upon the properties of stretched films. After stretching the films were dried in air fixed on the stretching apparatus. The tensile strength, elongation, Young's modulus, degree of double refraction and softened process of the stretched films were measured in the way stated in the previous reports.[2,6] Moreover the effects of polymerization degree on the above-mentioned properties of the stretched films of cellulose derivatives were investigated.

RESULTS AND CONSIDERATION

1. On Stretching

The cold drawing of high polymers was found out by W. H. Carothers and J. W. Hill.[7] They made it clear that very strong, pliable, highly orientated fibers similar closely to natural silk are obtained by stretching the linear condensation ω-polyesters, polyanhydrides and mixed polyester-polyamides. They also found that the necking of section area of a fiber occurs during cold drawing. We have many reports[8~13] in hand which deal with the necking. The necking also took place in stretching ethylcellulose films[3] in dry heated air, and part stretched at first showed a tendency to be stretched more on account of the necking of section area, and thus the stretched film was apt to be ununiform. This phenomenon seemed to occur because stretching has small effect on softening process of ethylcellulose. Of course this necking should occur in the case of stretching various high polymers films, but in many cases the part stretched at first, increased in resistance to stretching because of its advancement in resistance to temperature, and of increase in tensile strength of the part, and part not stretched at first, was then stretched and thus uniform stretching seemed to occur.

2. On Tensile Strength and Young's Modulus of Stretched Cellulose Derivative Films

Table 2. The Influence of Stretching in Dry Heated Air upon the Mechanical Properties of Cellulose Acetate Films

Degree of Stretching (Times)	Temperature of Stretching (°C)											
	215			225			235			245		
	T.S.	E.	Y.M.	T.S.	E.	Y.M.	T.S.	E.	Y.M.	T.S.	E.	Y.M.
1	6.0	10.6	163	6.0	10.6	163	6.0	10.6	163	6.0	10.6	163
1.5	14.1	6.9	296	12.2	11.6	188	8.0	11.3	218	5.3	13.9	207
2	18.2	6.0	476	14.0	11.1	297	8.4	10.8	296	5.0	13.9	209
3				17.2	7.2	405	13.3	10.0	384			
4				17.5	6.3	466	14.6	8.0	418			
5				19.3	5.4	727	23.3	7.6	583			
6							25.7	6.8	763			
7							25.5	6.7	704			

Abbreviations			
	T.S.	Tensile Strength	kg/mm^2
	E.	Elongation	%
	Y.M.	Young's Modulus	kg/mm^2

Table 3. The Influence of Stretching in Dry Heated Air upon the Mechanical Properties of Cellulose Acetate Films Containing Dimethylphthalate (DMP) 5%

Degree of Stretching (Times)	Temperature of Stretching (°C)														
	180			190			200			210			220		
	T.S.	E.	Y.M	T.S.	E.	Y.M.	T.S.	E.	Y.M.	T.S.	E.	Y.M.	T.S.	E.	Y.M.
1	7.8	17.5	104	7.8	17.5	104	7.8	17.5	104	7.8	17.5	104	7.8	17.5	104
1.2	12.4	15.7	236	12.5	16.3	195	11.9	18.3	146	11.0	18.1	137	11.4	18.1	118
1.5	17.4	10.7	291	17.4	13.4	245	17.9	14.0	228	18.7	14.5	231	19.7	13.9	220
2				(12.2	7.2	376)	24.2	11.3	361	24.2	11.6	325	24.4	11.7	342
2.5													18.3	6.4	458

Table 4. The Influence of Stretching in a Swelling Agent (Dioxane: Water=1:1) upon the Mechanical Properties of Cellulose Acetate Films (Temperature of Stretching: 25°C)

Degree of Stretching (Times)	Content of Dimethylphthalate (%)								
	0			1			5		
	T.S.	E.	Y.M.	T.S.	E.	Y.M.	T.S.	E.	Y.M.
1	6.0	10.6	163	7.9	16.6	91	7.8	17.5	104
1.2	—	—	—	10.3	29.3	53	11.6	30.8	92
1.5	7.0	11.5	250	12.1	22.9	124	13.8	23.6	127
2	11.2	9.1	494	16.1	19.0	151	19.3	14.0	241
2.5	14.3	6.8	545	19.6	14.5	248	22.4	13.3	299
3	15.9	5.7	582	23.0	13.4	309	27.5	12.0	421
4	21.1	5.8	854	27.4	12.9	423	35.3	10.1	567
5	23.2	5.1	961	32.6	11.6	540			
6	27.2	5.9	965	34.9	10.2	671			

Table 5. The Influence of Stretching in Dry Heated Air upon the Mechanical Properties of Ethylcellulose Films

Degree of Stretching (Times)	Temperature of Stretching (°C)								
	165			175			185		
	T.S.	E.	Y.M.	T.S.	E.	Y.M.	T.S.	E.	Y.M.
1	5.6	22.3	101	5.6	22.3	101	5.6	22.3	101
1.2	10.0	27.6	148	6.2	39.2	104	5.8	46.7	85
1.5	11.5	16.6	284	9.5	26.4	168	6.0	40.8	124
2	13.1	13.0	435	12.4	17.2	266	6.7	6.3	424
2.5	15.8	9.6	535	15.6	10.6	492	7.7	3.7	489
3	17.3	7.5	591	16.7	9.8	541			
4				19.1	7.5	613			

Table 6. The Influence of Stretching in Dry Heated Air upon the Mechanical Properties of Benzylcellulose Films

Degree of Stretching (Times)	Temperature of Stretching (°C)														
	120			130			140			150			160		
	T.S.	E.	Y.M.	T.S.	E.	Y.M.	T.S.	E.	Y.M.	T.S.	E.	Y.M.	T.S.	E.	Y.M.
1	4.4	14.3	39	4.4	14.3	39	4.4	14.3	39	4.4	14.3	39	4.4	14.3	39
1.2	5.3	14.5	45	5.3	15.6	31	5.2	18.7	29	4.5	14.8	47	4.3	14.2	39
1.5	6.5	14.2	54	6.2	14.1	43	5.4	15.4	32	4.7	26.4	36	4.1	17.6	37
2	6.7	11.7	84	6.7	12.7	82	5.9	13.9	47	4.9	17.5	45	3.6	27.3	35
2.5	6.7	10.4	116	7.1	11.8	98	6.3	12.8	52	4.9	17.1	51	3.2	16.6	53
3				7.5	11.2	114	6.6	12.3	69	5.0	13.4	72	2.4	13.5	79
4				8.3	9.2	139	7.8	11.5	93	5.3	11.7	104			
5				10.4	8.9	194	9.8	10.4	131						
6							10.2	8.6	171						

Table 7. 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			

Table 8. 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 9. The Changes of the Mechanical Properties of Carboxymethylcellulose Films by Stretching in Saturated Steam at Various Temperatures

Degee of Stretching (Times)	30°C			45°C		
	T. S.	E.	Y. M.	T. S.	E.	Y. M.
1	3.5	12.3	29	3.5	12.3	29
1.2	4.2	8.1	38	4.9	11.2	34
1.5	5.0	6.3	63	5.7	10.7	54
2.0	7.0	5.5	160	9.0	9.3	79
2.5				12.4	7.9	123

Table 10. The Changes of the Mechanical Properties of Cellulose Xanthate Filaments by Stretching under Various Conditions

Degree of Stre-tching (Times)	Stretching Temperature in 5% Na_2SO_4 Solution (°C)									Stretching in Water of 20°C		
	60			40			20					
	T.S.	E.	Y.M.	T.S.	E.	Y.M.	T.S.	E.	Y.M.	T.S.	E.	Y.M.
1	9.6	51.7	130	9.6	51.7	130	9.6	51.7	130	9.6	51.7	130
1.2	11.7	35.7	148	11.2	29.3	156	11.0	28.8	176	13.3	30.5	154
1.5	15.6	23.5	243	14.3	19.0	226	14.1	19.0	273	17.9	17.8	273
1.7	18.2	18.6	297	16.5	14.9	285	16.3	13.8	339	20.5	13.5	339
2	21.8	12.3	346	21.3	10.3	352	19.9	9.2	401	23.9	9.2	408

Tables 2, 3, 4, 5, 6, 7, 8, 9 and 10 give the changes in mechanical properties of the following films caused by stretching in various softened states. Cellulose acetate films, cellulose acetate films containing plasticizer, ethylcellulose films, benzylcellulose films, cellulose nitrate films, cellulose nitrate films containing camphor, carboxymethylcellulose films and cellulose xanthate filaments.

The tensile strength and Young's modulus increase, as a rule, with the degree of stretching. In the case of dry heated air stretching, the lower the temperature, and, in the case of swelling stretching, the higher the percentage of nonsolvent in a swelling agent, the higher the increasing rate of tensile strength and Young's modulus becomes. But in this case the possible degree of stretching is low because of the insufficient plasticity of films. On the contrary, in the case of dry heated air stretching, the higher the temperature, and, in the case of swelling stretching, the higher the percentage of solvent in a swelling agent, the lower the increasing rate of tensile strength and Young's modulus becomes, and there are even some cases where tensile strength and Young's modulus decrease with the degree of stretching. This fact indicates that the temperature in dry heated air stretching is too high for stretching or the swelling power is too large for swelling stretching.

The condition under which the highest degree of stretching is accomplished is the intermediate temperature, neither high nor low, in case of dry heated air stretching, and the intermediate composition of swelling agents, neither rich nor poor in solvent, in case of swelling stretching.

The highest tensile strength and the highest Young's modulus are accomplished either at the intermediate temperature or at the temperature a little lower than the intermediate in case of dry heated air stretching, and also at the composition of a swelling agent poorer in solvent than the intermediate in case of swelling stretching.

The change in Young's modulus of films caused by stretching shows, as a rule, the same tendency as that in the tensile strength, though a slight different tendency is seen in some kinds of cellulose derivative.

When these cellulose derivative films consisting of linear molecules are stretched at about the melting point or in a swelling agent, the molecules having many bending parts are stretched and orientated in the direction of stretching, and intermolecular slip and crystallization take place in some molecules, as seen in the measurement of the degree of double refraction. As a result the linear molecules come to have a stable structure. So we can be qualitatively convinced that the linear molecules which pass through the unit area at right angles to the direction of stretching increase in number with the degree of stretching, and thus that the tensile strength and Young's modulus are promoted in the direction of stretching but are decreased at right angles to the direction of stretching, with the degree of stretching.[14)]

Table 11. The Changes of Mechanical Properties of Cellulose Nitrate Films in Various Directions by Stretching in Acetone 2 :Water 1

Stretching Degree of (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

It seems that at too high temperature or in too large swelling power the movement of molecules becomes violent and molecules are on the one hand orientated to the direction of stretching and on the other hand they relax or slip one another, so the orientation of molecules does not become so good for the increasing degree of stretching. When the speed of stretching is made slow, in a swelling agent of low power i.e. in a state of poor plasticity, the films can be stretched up to high degree of stretching and their tensile strength and Young's modulus are increased.

This fact indicates that the slow speed of stretching contributes to the diffusion of a swelling agent into films and the intermolecular strain in stretching is removed and thus the molecules are brought into a stable orientation during a relatively long time of stretching.

When cellulose xanthate filaments made by natural flowing were stretched in air, water was squeezed out of the filaments and its drops were deposited on their surface, and so it is certain that, in the case of stretching high polymer films in a swelling agent, both the orientation of molecules and the squeeze of an agent take place.

Films increase in tensile strength by containing a little plasticizer. This seems to be due to the fact that the strain of molecules caused by intermolecular entanglement is relaxed by the containing of plasticizer and so the molecules come to the state that contributes to the tensile strength.

3. On Elongation of Stretched Cellulose Derivative Films

In the elongation-stretching degree curve, the writer could find the maximum point characteristic of stretching of high molecular compound films.

Elongation has a tendency to increase with stretching degree up to the maximum point, and from this point to decrease with stretching degree. This interesting fact was found at first in the stretched films of polyvinylchloride

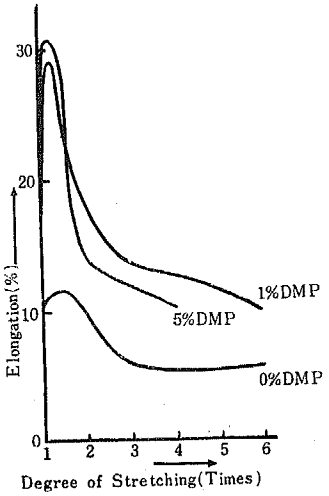

Fig. 1. The Change in Elongation of Cellulose Acetate Filmes Containing DMP by Stretching in a Swelling Agent of Dioxane 1 to Water 1 at 25°C

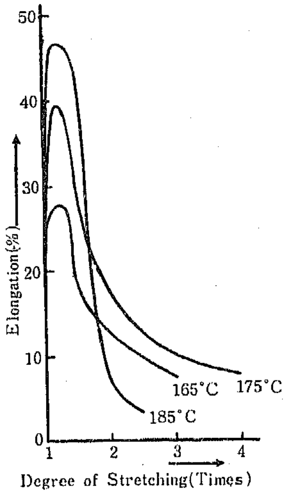

Fig. 2. The Change in Elongation of Ethylcellulose Films by Stretching in Dry Heated Air of Various Temperatures

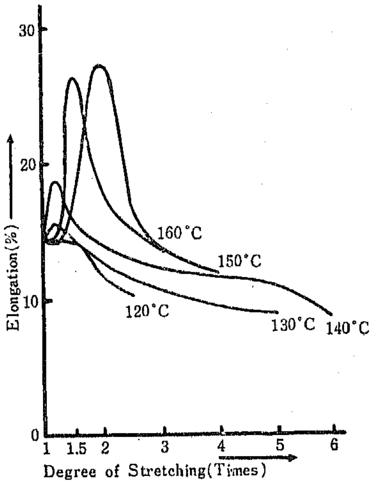

Fig. 3. The Change in Elongation of Benzylcellulose Films by Stretching in Dry Heated Air of Various Temperatures

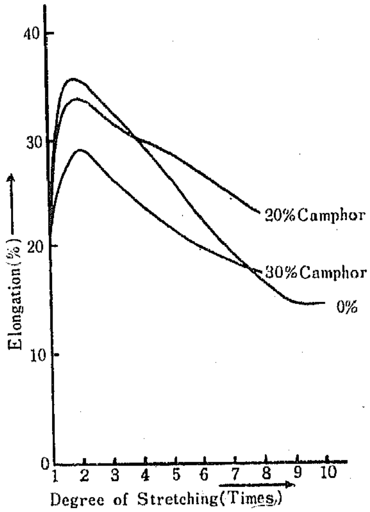

Fig. 4. The Change in Elongation of Cellulose Nitrate Films Containing Camphor by stretching in a Swelling Agent of Acetone 2 to Water 1 at 25°C

and polymethylmethacrylate by Dr. Sakurada,[15] and was later found in the films of various synthetic high compounds by Funahashi.[16] The writer found it also in the films of various cellulose derivatives, as seen in Tables 2, 3, 4, 5, 6, 7 and 8 and Figs. 1, 2, 3 and 4. In the case of cellulose derivatives, however, the maximum point is not so distinguished as in the case of synthetic high molecular compounds.

Lohmann[14] has reported on the change in mechanical properties of cellulose acetate filaments by stretching in a swelling agent of dioxane 1 to water 1. According to his results, the above-mentioned maximum point cannot be found as seen in Fig. 5.

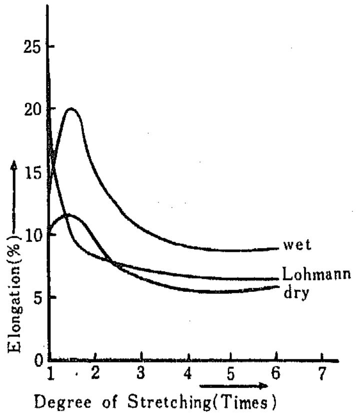

Fig. 5 The Change in Elongation of Cellulose Acetate Films and Filaments by Stretching in a Swelling Agent of Dioxane 1 to Water 1

The result on cellulose acetate films is also shown in Fig. 5. In Fig. 5, when Lohmann's 1 time point is carried to our 1.5 times point, both elongation curves coincide with each other. So this fact indicates that in Lohmann's cellulose acetate filaments, linear molecules are a little orientated in the direction of filament.

The maximum point is higher in films stretched in an agent rich in solvent than in those in an agent poor in solvent, and the position of the maximum point seems to move slightly to the higher degree of stretching according as the swelling agent becomes richer in solvent or as the stretching temperature becomes higher. When compared at the same degree of stretching, the elongation of films stretched in an agent rich in solvent is higher than that in an agent poor in solvent. The stretching condition under which the maximum point of elongation gives the highest value seems to be the composition of higher swelling power or the higher temperature than the condition under which possible degree of stretching becomes the highest.

But in case of carboxymethylcellulose films and cellulose xanthate filaments, this maximum point is not found. This fact seems to be due to the shape of their molecules relatively more extended than that of synthetic high compounds, and to the relatively larger intermolecular force in cellulose derivative films than in synthetic high polymer films. Carboxymethylcellulose and cellulose xanthate are polyelectrolytes. So their molecules seem to be in considerably stretched shape in their solutions because of the repulsion of ions in polyionic molecules, and to be fixed as the stretched shape when films are made from their solutions. Moreover, as there is water, as a component, in swelling agents at the time of stretching their films in a swollen state, the ions possess Na^+ ions in common between molecules or micelles and have influence on each other with no small forces in the same way with hydrogen bond, and thus knots in the net structure seem to be formed there. Of course, all of their ions do not form such knots and it seems that formed knots are not so strong as they are not influenced by stretching. But the possible degree of stretching is 2 times in case of cellulose xanthate filaments and is 2.5 times in case of carboxymethylcellulose films, so it seems that considerable force acts between molecules.

According to P. H. Hermans net structure theory,(7) the maximum degree of stretching is 1.73 times in his first model i. e. in the cubic space net structure that consists of rods combined at cubic corners so as to be able to act mutually, and the maximum degree is 2 times in his second model i. e. in the net structure in which micelles are connected lengthwise and breadthwise with one another by subvalency union in fringe parts extended in the shape of a fan. If we suppose the net structure similar to the P. H. Hermans second model, it can be explained that the possible degree of stretching is from 2 to 2.5 times and the maximum point cannot be found in the elongation-stretching degree curves.

In cellulose xanthate isotropic filaments and carboxymethylcellulose films, amorphous parts exist predominantly rather than micelle parts, so molecular nets of ions will exist in place of nets of micelles, though the P. H. Hermans model is a net structure of micelles. Thus in case of stretching carboxymethylcellulose films and cellulose xanthate filaments, the mechanism of stretching seems to be quite different from that in case of stretching the other cellulose derivative films. Of course, if carboxymethylcellulose films and cellulose xanthate filaments had plasticity in the state under which their strong subvalency would act mutually on, as in case of stretching polyvinylalcohol films[18] in dry heated air, they could be stretched to high degree and be treated in the similar way to the other general stretching.

The following are the results and consideration on stretching cellulose derivative films excepting above-mentioned polyelectrolytes. Let us discuss the state under which stretched films show high elongation, and the characteristics of the elongation. Figs. 6, 7, 8, 9 and 10 give stress-elongation curves in case of films of various cellulose derivatives, indicating the sta-

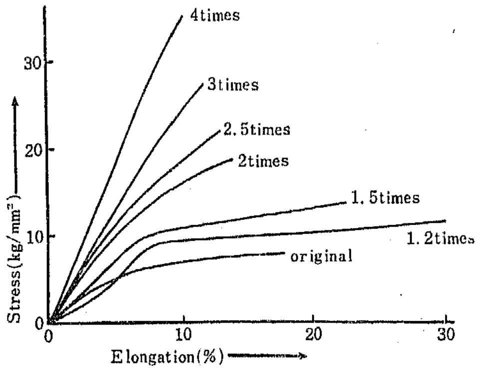

Fig. 6. Stress–Elongation Curves of Cellulose Acetate Stretched Films Containing 5% DMP

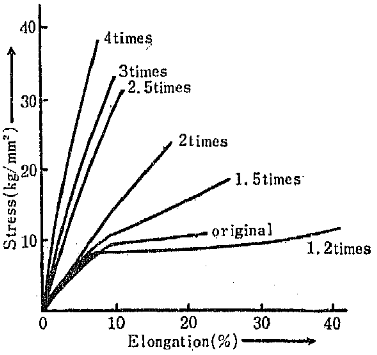

Fig. 7. Stress–Elongation Curves of Ethylcellulose Films Stretched at 175°C in Dry Heated Air

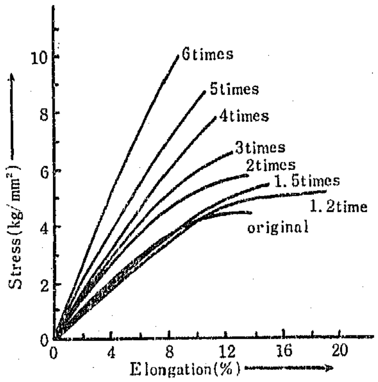

Fig. 8. Stress–Elongation Curves of Benzylcellulose Films Stretched at 140°C in Dry Heated Air

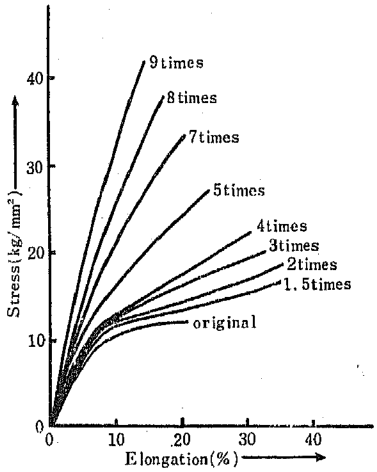

Fig. 9. Stress–Elongation Curves of Cellulose Nitrate Films Stretched in a Swelling Agent of Acetone 2 to Water 1 at 25°C

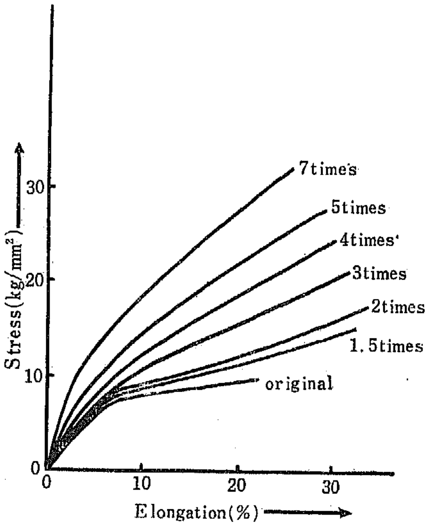

Fig. 10. Stress-Elongation Curves of Cellulose Nitrate Stretched Films Containing 20% Camphor
(Films Stretched in a Swelling Agent of Acetone 2 to Water 1 at 25°C)

tes of elongation appearing in stretched films and unstretched films. Even in the films of over 40% elongation, the state of elongation appearance has a different aspect from that in melted state or in softened state by a softening agent. In the figures, the curves are almost in straight lines without exception up to certain stress, from which they suddenly begin to be high in elongation passing a distinct yielding point, and this yielding point becomes indistinct gradually with the increasing degree of stretching.

In case of almost all synthetic high molecular compounds, for example, polyvinylchloride and polyvinylalcohol etc., the original films are broken in the neighbourhood of the yielding point i.e. at the place where elongation suddenly starts becoming high, but in case of cellulose derivatives the original films are extended to a considerable length after the distinct yielding point. From this point of view, the original films of cellulose derivatives correspond to the films in which the effect of stretching is apparent. This is the cause for the fact that the maximum point of elongation in cellulose derivative films is less distinct than that in synthetic high molecular compounds films.[16] It seems to prove that the molecules of cellulose derivatives are in relatively extended form in their films.

In case of synthetic high molecular compounds,[16] the more brittle the films generally are, the higher the stretching degree corresponding to the maximum point of elongation becomes. In case of cellulose derivatives, the films are in a state of begining to be elongated by a little orientation effect owing to the complexity of their molecules, so almost all of their maximum points are at the low degree of stretching i.e. 1.2 to 1.5 times stretching degree.

Moreover the maximum point of elongation in cellulose acetate films becomes distinct by the containing of dimethylphthalate. When films contain plasticizer, their elongation generally becomes higher and furthermore the elongation of stretched films is more elevated than that of the original films, thus it seems that the maximum point in films containing plasticizer becomes distinct. In case that the load is not too heavy for films in the experiment on their softening process, the original films give the highest elongation. Judging from this fact, the original films are expected to give the maximum elongation at high temperature in the neighbourhood of the softening point. It can be considered that the maximum point in the elongation-stretching degree curve is not a fixed point, but a point varing according to measuring temperature. In fact, when the change of elongation of ethylcellulose films stretched at 175°C is measured at −20°C, 0°C, 20°C respectively, the maximum point of elongation moves to the high degree of stretching according to the lowering of measuring temperature, as seen in Fig. 11.

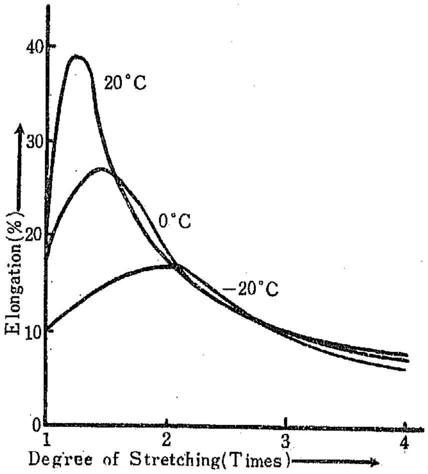

Fig. 11. The Change in Elongation of Ethylcellulose Films Stretched at 175°C in Dry Heated Air by Changing Measuring Temperature

In taking the above-mentioned facts into mature consideration, the cause for the existence of the maximum point in the elongation-stretching degree curve seems to be qualitatively what follows. Namely, linear molecules in the original films are in a state of the maximum degree of bending, but at 20°C of measuring temperature they break before their bending extends and thus the elongation appears. However, in case of the films in which the molecules are a little orientated in the direction of stretching by some degree of stretching, the intermolecular force is able to tend to full extension of the bent molecules and thus high elongation comes to appear.

4. On the Heat Softening Process

Table 12. The Change (%) in the Elongation of Cellulose Acetate Films under Various Loads by Heating

Temperature (°C)	Load (kg/mm²)				
	1.0	0.8	0.5	0.1	0.05
80	0.2	—	—		
90	—	0.2	—		
100	0.4	0.3	0.1		
110	0.6	—	—		
120	0.9	0.6	0.3	0.1	
130	1.2	—	—	—	
140	1.6	0.9	0.6	—	
150	2.0	1.1	0.9	—	
160	2.6	1.6	1.3	0.2	0.1
170	3.1	2.2	1.6	—	—
180	4.1	2.9	2.3	—	—
190	6.3	4.5	3.3	0.3	—
200	8.6	5.9	4.3	0.4	0.2
205	10.9	7.5	—	—	—
210	14.1	9.8	5.9	0.8	0.3
215	21.1	15.0	8.8	1.0	—
220	39.0	27.5	16.5	1.9	0.4
225	>100	48.6	34.8	4.1	0.6
230		>100	65.8	6.8	1.5
235			>100	10.8	3.1
240				63.4	8.2
245				>100	24.9
250					>100

Table 13. The Change (%) in the Elongation of Cellulose Acetate Stretched Films under 0.5 kg/mm² Load by Heating (Films Stretched at 235°C in Dry Heated Air)

Temperature (°C)	Degree of Stretching (Times)								Cellulose Acetate Filament
	1	1*	1.2	1.5	2	3	4	5	
100	0.1	0.2							
120	0.3	—							
130	—	—							
140	0.6	—							
150	0.9	—							
160	1.3	0.5	0.1						
170	1.6	—	—						0.2
180	2.3	—	0.3						

190	3.3	1.0	—						—
200	4.3	1.3	0.6	0.1					0.4
205	—	—	0.8	—					
210	5.9	1.7	1.1	0.3	0.1				0.7
215	8.8	3.4	1.8	0.5	—				1.3
220	16.5	5.0	2.5	1.0	0.4				2.0
225	34.8	13.7	5.9	1.8	—	−0.1	−0.1	−0.1	5.6
230	65.8	28.3	18.3	4.9	0.6	−0.3	−0.4	−0.5	14.6
235	>100	51.6	37.8	16.1	1.5	−0.6	−0.9	−0.9	35.0
240		>100	62.1	30.5	3.4	−0.1	−1.0	−1.4	58.1
245			>100	61.2	16.0	1.2	−0.5	−1.6	>100
250				>100	32.5	3.1	±0	−1.1	
255					76.8	10.5	2.0	−0.4	
260					>100	29.3	8.7	1.0	
265						78.8	16.4	3.5	
270						(Breaking)	47.6	10.3	
275							(Breaking)	22.6	
								(Breaking)	

* Films Heated at 235°C for 10 Minutes

Table 14. The Change in the Elongation of Ethylcellulose Stretched Films under 0.25 kg/mm² Load by Heating
(Films Stretched at 175°C in Dry Heated Air)

Temperature (°C)	Degree of Stretching (Times)						
	1	1.2	1.5	2	2.5	3	4
100	0.1						
110	0.6	0.1					
120	1.1	—	0.2				
130	2.1	0.7	—	0.2			
135	—	—	0.6	—	0.2		
140	3.6	1.1	—	0.6	0.4	0.2	
145	5.0	2.0	1.9	—	—	—	0.2
150	8.3	4.0	3.1	1.8	1.0	0.6	0.3
155	12.6	9.6	4.5	—	—	0.9	0.5
160	21.3	18.0	8.4	3.2	1.9	1.5	0.7
165	42.4	36.5	22.1	10.8	4.1	2.7	1.0
170	>100	>100	51.2	32.6	9.4	5.0	2.3
175			>100	81.1	37.5	9.6	5.1
180				>100	93.8	20.9	11.5
185					(Breaking)	76.4	66.2
190						(Breaking)	(Breaking)

Table 15. The Change in the Elongation of Benzylcellulose Stretched Films under 0.1 kg/mm² Load by Heating (Films Stretched at 140°C in Dry Heated Air)

Temperature (°C)	Degree of Stretching (Times)							
	1	1.5	2	2.5	3	4	5	6
70	0.1							
80	0.3							
90	0.6	0.2						
100	1.1	0.4						
105	3.2	0.8	0.1					
110	7.4	1.4	0.3	0.2				
115	13.5	2.8	0.9	0.5	0.3			
120	32.9	5.4	1.8	0.9	0.7	0.2		
125	>100	10.1	3.7	2.5	1.9	0.5		
130		30.6	7.7	5.4	3.1	1.2	0.2	
135		>100	36.1	9.2	5.0	1.9	1.3	0.3
140			>100	19.6	9.3	3.5	2.0	0.7
145				>100	20.4	6.3	3.2	1.5
150					>100	11.7	5.1	2.1
155						21.1	10.3	4.2
160						>100	17.7	6.5
165							35.4	10.1
170							86.7	22.7
175							(Breaking)	56.0 (Breaking)

Table 16. The Percentage of Heat Shrinkage of Cellulose Acetate Stretched Films at Various Temperatures (Films Stretched at 235°C in Dry Heated Air)

Degree of Stretching (Times)	Temperature (°C)						
	220	225	230	235	240	245	250
1		(1.0)	(2.0)	(5.0)	(12.0)	(13.0)	(15.0)
2	2.0	5.0	7.0	16.0	36.0	60.0	86.2
3	1.2	2.1	3.0	13.4	33.2	50.4	63.2
4	0.7	1.3	1.7	8.7	24.0	48.3	57.7
5		0.3	0.5	7.5	26.5	47.5	55.0
6		0.4	0.8	5.0	24.0	44.2	52.2
7		0.4	0.7	4.7	11.7	30.8	44.1

Table 17. The Percentage of Heat Shrinkage of Cellulose Acetate Stretched Films at Various Temperatures
(Films Stretched in a Swelling Agent of Dioxane 1 to Water 1)

Degree of Stretching (Times)	Temperature (°C)						
	220	225	230	235	240	245	250
1		(1.0)	(2.0)	(5.0)	(12.0)	(13.0)	(15.0)
2	2.1	4.3	10.1	35.2	53.4	68.0	77.2
3	0.5	2.5	7.5	17.0	31.0	48.5	55.5
4		1.3	7.0	14.3	26.7	36.7	48.3
5			0.5	9.7	17.0	32.5	44.5
6				4.0	14.6	30.8	34.2
7					2.8	24.7	31.7

Tables 12, 13, 14, 15, 16 and 17 show the changes in the elongation of various cellulose derivative films under certain loads by heating. Heating is done at a constant rate of 5°C/min. because it gives considerable effect on molecules in films. The effect of stretching on the heat softening process of cellulose derivative films is almost none or a little if any. This seems to be due to the fact that in case of cellulose derivatives the molecules in their films are not crystallized but are orientated by means of stretching, and proves that the orientation of molecules in the films has almost no effect on their resistance to temperature. From the experiments in which the stretched films are shrunk in dry heated air or in a swelling agent, it is clear, as seen in Tables 16 and 17, that intermolecular sliding takes place in some degree when films are stretched.

Table 18. The Mechanical Properties of Cellulose Acetate Shrunk Films
(Films shrunk in a Swelling Agent of Dioxane 1 to Water 1 at 25°C)

Degree of Stretching (Times)	Films Stretched in Dry Heated Air				Films Stretched in a Swelling Agent			
	Before Shrinkage		After Shrinkage		Before Shrinkage		After Shrinkage	
	T.S.	E.	T.S.	E.	T.S.	E.	T.S.	E.
1	6.0	10.6			6.0	10.6		
1.5	8.0	11.3	8.1	8.3	7.0	11.5	6.3	7.1
2	8.4	10.8	10.5	10.6	11.2	9.1	8.1	12.8
3	13.3	10.0	12.4	8.9	15.9	5.7	12.5	17.6
4	14.6	8.0	12.6	7.4	21.1	5.8	15.8	14.2
5	23.3	7.6	15.8	5.8	23.2	5.1	22.5	14.7
6	25.7	6.8	15.8	6.3	27.2	5.9	26.6	12.2
7	25.5	6.7	15.0	6.6	(110.1)	(11.8)	30.2	11.3

Moreover, it has been affirmed that cellulose derivative stretched films are prevented, as seen in Table 18, from becoming lower in elongation, which is a weak point in stretching, by their shrinkage in dry heated air or in a swelling agent.

5. On Double Refraction

Table 19. The Double Refraction of Various Cellulose Acetate Films Stretched in a Swelling Agent of Dioxane 1 to Water 1

(A) Films Containing no Plasticizer

Degree of Stretching	1	1.5	2	3	4	5	6
$n\gamma-n\alpha$	0.000	0.0012	0.0029	0.0054	0.0078	0.0088	0.0096
T. S.	6.0	7.0	11.2	15.9	21.1	23.2	27.2

(B) Films Containing 1% Dimethylphthalate

Degree of Stretching	1	1.2	1.5	2	2.5	3	4	5	6
$n\gamma-n\alpha$	0.000	0.00114	0.00236	0.00336	0.0038	0.0043	0.00535	0.0062	0.0068
T. S.	7.9	10.3	12.1	16.1	19.6	23.0	27.4	32.6	34.9

(C) Films Containing 5% Dimethylphthalate

Degree of Stretching	1	1.2	1.5	2	2.5	3	4
$n\gamma-n\alpha$	0.000	0.00093	0.0023	0.0037	0.00436	0.0054	0.0068
T. S.	7.8	11.6	13.8	19.3	22.4	27.5	35.3

C=0.7576

Table 20. The Double Refraction of Ethylcellulose Films Stretched in Dry Heated Air at 175°C

Degree of Stretching	1	1.2	1.5	2	3	4
$n\gamma-n\alpha$	0.000	−0.0038	−0.0112	−0.0200	−0.0301	−0.0358
T. S.	5.6	6.2	9.5	12.4	16.7	19.1

C=0.7576

Table 21. The Double Refraction of Benzylcellulose Films Stretched in Dry Heated Air at Various Temperatures

(A) Stretching at 160°C

Degree of Stretching	1	1.2	1.5	2	2.5	3
$n\gamma-n\alpha$	0.000	0.0010	0.0020	0.0018	0.0016	0.0012
T. S.	4.4	4.3	4.1	3.6	3.2	2.4

(B) Stretching at 150°C

Degree of Stretching	1	1.2	1.5	2	2.5	3	4
$n\gamma-n\alpha$	0.000	0.0012	0.0034	0.0035	0.0034	0.0035	0.0040
T. S.	4.4	4.5	4.7	4.9	4.9	5.0	5.3

(C) Stretching at 140°C

Degree of Stretching	1	1.2	1.5	2	2.5	3	4	5	6
$n\gamma-n\alpha$	0.000	0.0039	0.0043	0.0049	0.0056	0.0063	0.0080	0.0093	0.0094
T. S.	4.4	5.2	5.4	5.9	6.3	6.6	7.8	8.8	10.2

(D) Stretching at 130°C

Degree of Stretching	1	1.2	1.5	2	2.5	3	4	5
$n\gamma-n\alpha$	0.000	0.0035	0.0049	0.0062	0.0069	0.0075	0.0090	0.0099
T. S.	4.4	5.3	6.2	6.7	7.1	7.5	8.3	10.4

(E) Stretching at 120°C

Degree of Stretching	1	1.2	1.5	2	2.5
$n\gamma-n\alpha$	0.000	0.0035	0.0069	0.0079	0.0081
T. S.	4.4	5.3	6.5	6.7	6.7

$C=0.7576$

Table 22. The Double Refraction of 30% Camphor Contained 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	0.0019	0.0025	0.0031	0.0036	0.004	0.0042	0.0045	0.0045	0.0044	0.0043
T. S.	7.2	7.9	9.0	10.7	13.2	14.9	15.7	17.2	17.2	17.1	17.0

(B) Stretching in Acetone : Water = 2 : 1

Degree of Stretching	1	1.5	2	3	4	5	6	7	8
$n_\gamma - n_\alpha$	0.000	0.0028	0.0034	0.0043	0.005	0.0058	0.0065	0.0065	0.0066
T. S.	7.2	10.3	12.8	15.7	19.7	23.1	25.5	25.3	25.9

(C) Stretching in Acetone : Water = 3 : 2

Degree of Stretching	1	1.5	2	2	4
$n_\gamma - n_\alpha$	0.000	0.003	0.0038	0.0046	0.0052
T. S.	7.2	11.3	14.5	17.4	20.9

C = 0.7576

Tables 19, 20, 21 and 22 show the degree of double refraction of various cellulose derivative stretched films. The degree of double refraction19) is calculated from the following equation.

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

where $n_\gamma - n_\alpha$: degree of double refraction
d : thickness of films
c : compensator constant
Γ : retardation

The degree of double refraction increases as a rule with stretching degree and the increasing state is parallel to that of tensile strength. When the orientation of molecules or micelles in films is disturbed by the strong power of a swelling agent at a high stretching degree, both the tensile strength and the degree of double refraction decrease with the degree of stretching.

It is very interesting that the relation between tensile strength and degree of double refraction in the same material is shown with the same two straight lines jointed, regardless of the condition of stretching, as seen in Fig. 12 and Fig. 13. Namely, in the same material, when the degree of double refraction is the same, the tensile strength is the same in value. Generally speaking, the more the content of plasticizer, the lower the degree of double refraction becomes, but the tensile strength is increased by the containing of plasticizer as long as its content is a little.

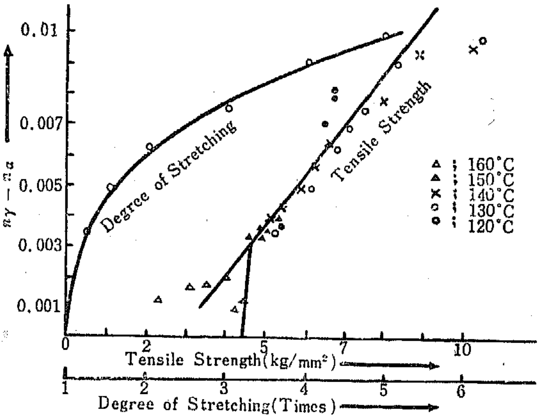

Fig. 12. Relation of the Degree of Double Refraction to the Tensile strength and Stretching Degree in case of Benzylcellulose Films Stretched in Dry Heated Air at Various Temperatures

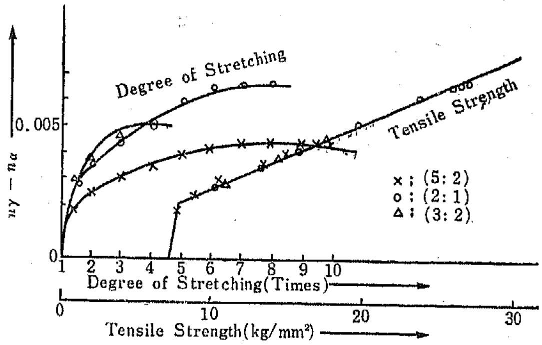

Fig. 13. Relation of the Degree of Double Refraction to the Tensile Strength and Stretching Degree in case of 30% Camphor Contained Cellulose Nitrate Films Stretched in Various Swelling Agents of Acetone to water

6. The Effect of the Polymerization Degree of Various Cellulose Derivatives on their Properties[20)21)]

The fractionated cellulose derivatives[22)23)24)] used in this chapter are shown in Tables 23 and 24. Fractionation was done by the fractional precipitation as reported in the previous[4)5)] paper. The measurements of their properties[25)] are shown in Tables 25, 26 and 27.

Table 23. Various Properties of Fractionated Cellulose Acetate

No. of Sample	Yield (%)	Intrinsic Viscosity [η] (100ml/g)	Degree* of Polymerization	T. S.	E.	Y. M.
Original	100	1.42	158**	7.9	15.6	117
Fr. 1 No. 2	9.4	2.083	304	15.1	22.2	128
Fr. 2 No. 2	12.5	1.666	243	13.9	19.8	126
Fr. 3 No. 1	18.8	1.372	200	12.8	18.9	123
Fr. 4 No. 1	8.8	0.965	139	9.8	12.9	126
Fr. 4 No. 3	5.9	0.762	111	6.2	11.3	117
Fr. 5 No. 1	1.2	0.657	96	5.0	7.5	85

* Degree of polymerization is calculated by using $a=1.0$, $K=2.54\times10^{-5}$ in $[\eta]=KM^{a}$

** This value is obtained by $Km=9\times10^{-4}$ in $[\eta]=KmP$

Table 24. Various Properties of Fractionated Cellulose Nitrate

No. of Sample	Yield (%)	Intrinsic Viscosity [η] (100ml/g)	Degree * of Polymerization	T. S.	E.	Y. M.
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 N0. 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

* Degree of polymerization is calculated by using $Km=10\times10^{-4}$ in $[\eta]=KmP$.

Table 25. Mechanical Properties of Fractionated Cellulose Acetate Films Stretched in a Swelling Agent of Dioxane 1 to Water 1 at 25°C

Degree of Stretching (Times)	Original			P = 304			P = 243		
	T. S.	E.	Y. M.	T. S.	E.	Y. M.	T. S.	E.	Y. M.
1	7.9	15.6	117	15.1	22.2	128	13.9	19.8	126
1.2	11.3	18.5	128	19.9	27.7	141	16.2	28.3	140
1.5	13.9	15.5	136	24.8	24.7	175	19.4	25.9	182
2	17.1	13.1	229	28.4	18.2	234	26.0	19.9	256
2.5	—	—	—	36.3	16.0	279	29.9	16.5	302
3	20.2	10.7	320	43.8	14.8	351	34.6	14.9	417
4	23.3	9.9	387	49.9	13.8	468	44.2	13.6	522
5	27.7	8.6	553	52.7	13.0	595	48.2	12.6	640
6				56.0	12.3	702	52.2	12.3	768
7				58.3	11.2	822	51.4	11.1	895
8				61.2	10.8	936			

Degree of Stretching (Times)	P=200			P=139			P=111		
	T.S.	E.	Y.M.	T.S.	E.	Y.M.	T.S.	E.	Y.M.
1	12.8	18.9	123	9.8	12.9	126	6.2	11.3	117
1.2	13.6	33.4	138	11.2	20.6	134	7.3	11.7	129
1.5	16.7	27.6	173	15.1	16.6	202	9.2	11.2	133
2	23.3	24.2	230	20.2	14.5	315	11.9	9.8	235
2.5	26.8	18.0	288	22.6	12.4	393			
3	30.4	15.2	415	24.1	11.4	489			
4	41.9	13.7	536	27.0	9.4	730			
5	46.0	12.4	691	31.2	8.8	899			
6	48.1	11.9	828						
7	48.3	11.4	966						

Table 26. Mechanical Properties of Fractionated Cellulose Nitrate Films Stretched in a Swelling Agent of Acetone 2 to Water 1 at 25°C

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			

Table 27. The Changes of Various Properties of Fractionated Cellulose Acetate Films Caused by Alkali Saponification
(Stretching in a Swelling Agent of Dioxane 1 to Water 1 at 25°C ; Saponification in 1N NaOH Solution Containing 20% Sodium Tartrate at 80°C.)

Degree of Stretching	Before Saponification			After Saponification			The Latter to The Former		
	T.S.	E.	Y.M.	T.S.	E.	Y.M.	T.S. (Times)	E. (Times)	Y.M. (Times)
(A) Fr. 1, No. 2 (P=304)									
1	15.1	22.2	128	25.3	32.7	384	1.67	1.47	3.00
1.2	19.9	27.7	141	27.1	28.8	437	1.37	1.04	3.10
1.5	24.8	24.7	175	40.5	23.3	526	1.63	0.94	3.01
2	28.4	18.2	234	47.5	16.4	702	1.68	0.90	3.00
2.5	36.3	16.0	279	58.3	14.1	852	1.61	0.88	3.05
3	43.8	14.8	351	67.6	12.6	970	1.54	0.85	2.76
4	49.9	13.8	468	80.2	11.7	1350	1.61	0.85	2.89
5	52.7	13.0	595	86.6	11.3	1625	1.64	0.87	2.73
6	56.0	12.3	702	91.3	10.5	1810	1.63	0.85	2.58
7	58.3	11.2	822	103.1	9.9	2100	1.77	0.88	2.55
8	61.2	10.8	936	117.8	9.8	2380	1.92	0.91	2.54
(B) Fr. 2, No. 2 (P=243)									
1	13.9	19.8	126	19.8	26.5	300	1.43	1.34	2.38
1.2	16.2	28.3	140	23.4	24.1	362	1.44	0.85	2.58
1.5	19.4	25.9	182	28.5	19.8	515	1.47	0.77	2.83
2	26.0	19.9	256	37.2	15.2	666	1.43	0.76	2.60
3	34.6	14.9	417	52.7	12.2	980	1.52	0.82	2.35
4	44.2	13.6	522	66.1	10.2	1330	1.50	0.75	2.55
5	48.2	12.6	640	72.5	10.1	1500	1.50	0.80	2.35
6	52.2	12.3	768	80.8	9.3	1650	1.55	0.76	2.15
7	51.4	11.1	895	90.7	9.0	2097	1.76	0.81	2.34
(C) Fr. 4, No. 1 (P=139)									
1	9.8	12.9	126	15.9	19.1	343	1.62	1.48	2.72
1.5	15.1	16.6	202	23.9	14.7	568	1.58	0.89	2.81
2	20.2	14.5	315	30.9	12.6	721	1.53	0.87	2.29
2.5	22.6	12.4	393	35.1	10.5	928	1.57	0.85	2.36
3	24.1	11.4	489	38.2	9.9	1200	1.59	0.87	2.45
4	27.0	9.4	730	43.9	8.9	1540	1.62	0.95	2.11
5	31.2	8.8	899	51.4	8.0	1900	1.65	0.91	1.12
(D) Fr. 4, No. 3 (P=111)									
1	6.2	11.3	117	10.1	11.8	132	1.63	1.04	1.13
1.5	9.2	11.2	133	15.5	10.6	193	1.69	0.95	1.44
2	11.9	9.8	235	17.0	9.0	278	1.43	0.92	1.23

Within the limit of the polymerization degree used in this paper i.e. up to a polymerization degree of about 300, the tensile strength and Young's modulus are remarkably increased with the degree of polymerization. It is recognized, however, that the rate of increasing in the properties caused by the increasing in polymerization degree becomes slow in case of the polymerization degree of over 200. The mechanical properties of fractionated cellulose derivative films have advantages over those of unfractionated films because the former is uniform in polymerization degree by fractionation.

It is widely known that, in case of the polar compounds of which intermolecular action is strong, for example polyvinylalcohol, polyamide[26] and cellulose xanthate etc., tensile strength becomes advantageous by the containing of low molecular parts because they act as a plasticizer in films or filaments. Spurlin[27][28] also recognizes that in case of cellulose nitrate the tensile strength is elevated by the containing of the low molecular parts of a polymerization degree of 100 to 160, though it is decreased by the containing of the parts of a polymerization degree of below 50. But in case of cellulose derivative films, the more uniform the polymerization degree is, the more the tensile strength is increased, and the stretching effect is advantageous by not containing the parts of low polymerization degree. This seems to be due to the fact that in case of cellulose derivative films hydroxyl groups in cellulose molecules are covered with various radicals and their polarity is relatively weak and the intermolecular force is small, and therefore molecular orientation easily takes place by deformation and thus the addition of low polymerization degree parts to act as plasticizer to the films is meaningless. And also that in cellulose derivative films the existence of many molecules higher than a certain degree of polymerization is advantageous to their tensile strength because combination force by principal valency has a predominant meaning for their tensile strength.

In case of the unstretched films of various cellulose derivatives, the relation of polymerization degree, P, to tensile strength, F, can be expressed by the following equation,[29] and the relation of F·P to P is shown with a straight line.

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

where A or B = a constant

The effect of the polymerization degree on the softening process exists a little as long as the polymerization degree of films is low and seems to come to almost nothing in high degree of polymerization.

Tables 28, 29 and 30 show the measurements of double refraction of the stretched films of fractionated cellulose derivatives. Generally speaking, within the limit of polymerization degree used in this experiment, the higher the polymerization degree, the higher the degree of double refraction

Table 28. The Double Refraction of Fractionated Cellulose Acetate Films Stretched in a Swelling Agent of Dioxane 1 to Water 1 at 25°C

P=304

Degree of Stretching	1	1.2	1.5	2	2.5	3	4	5	6	7	8
$n_\gamma - n_\alpha$	0.000	0.0020	0.0043	0.0052	0.0070	0.0085	0.00984	0.0107	0.0117	0.01235	0.0128
T. S.	15.1	19.9	24.8	28.4	36.3	43.8	49.9	52.7	56.0	58.3	61.2

P=243

Degree of Stretching	1	1.2	1.5	2	2.5	3	4	5	6	7
$n_\gamma - n_\alpha$	0.000	0.00197	0.0038	0.0051	0.00625	0.00735	0.0094	0.0105	0.01155	0.0125
T. S.	13.9	16.2	19.4	26.0	29.9	34.6	44.2	48.2	52.2	51.4

P=200

Degree of Stretching	1	1.2	1.5	2	2.5	3	4	5	6	7
$n_\gamma - n_\alpha$	0.000	0.0014	0.0035	0.0049	0.0057	0.0066	0.0095	0.0105	0.01115	0.0119
T. S.	12.8	13.6	16.7	23.3	26.8	30.4	41.9	46.0	48.1	48.3

P=139

Degree of Stretching	1	1.2	1.5	2	2.5	3	4	5
$n_\gamma - n_\alpha$	0.000	0.0022	0.00335	0.00475	0.0053	0.0058	0.00675	0.00785
T. S.	9.8	11.2	15.1	20.2	22.6	24.1	27.0	31.2

P=111

Degree of Stretching	1	1.2	1.5	2
$n_\gamma - n_\alpha$	0.000	0.0012	0.0020	0.0028
T. S.	6.2	7.3	9.2	11.9

C=0.7576

Table 29. The Double Refraction of Fractionated Cellulose Nitrate Films Stretched in a Swelling Agent of Acetone 2 to Water 1 at 25°C

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=0.7576

Table 30. The Change of the Degree of Double Refraction of Stretched Cellulose Acetate Films Caused by Alkali Saponification
(Saponification in 1N NaOH Solution Containing 20% Sodium Tartrate at 80°C)

P=304

Degree of Stretching	1	1.2	1.5	2	2.5	3	4	5	6	7	8
$n\gamma-n\alpha$	0.0121	0.0176	0.0228	0.0257	0.0298	0.0315	0.0338	0.0372	0.0384	0.0406	0.0425
T. S.	25.3	27.1	40.5	47.5	58.3	67.6	80.2	86.6	91.3	103.1	117.8
$n\gamma-n\alpha$ before Saponification	0.000	0.002	0.0043	0.0052	0.0070	0.0085	0.00984	0.0107	0.0117	0.01235	0.0128

P=243

Degree of Stretching	1	1.2	1.5	2	3	4	5	6	7
$n\gamma-n\alpha$	0.0087	0.0169	0.0218	0.0238	0.0273	0.0315	0.0344	0.0368	0.0371
T. S.	19.8	23.4	28.5	37.2	52.7	66.1	72.5	80.8	90.7
$n\gamma-n\alpha$ before Saponification	0.000	0.00197	0.0038	0.0051	0.00735	0.0094	0.0105	0.01155	0.0125

$P=139$

Degree of Stretching	1	1.5	2	2.5	3	4	5
$n\gamma-n\alpha$	0.0063	0.01595	0.0172	0.0176	0.01885	0.0210	0.0229
T. S.	15.9	23.9	30.9	35.1	38.2	43.9	51.4
$n\gamma-n\alpha$ before Saponification	0.000	0.00335	0.00475	0.0053	0.0058	0.00675	0.00785

$C=0.7576$

becomes, and the highest degree of double refraction is obtained in high degree of stretching. This is clear from the fact that the curve of tensile strength is in parallel with that of the degree of double refraction.

Under the same polymerization degree, the relation between tensile strength and the degree of double refraction is shown with two straight lines jointed, and when tensile strength decreases with the degree of stretching, the degree of double refraction also decreases with it. Under the same tensile strength the lower the polymerization degree, the higher the degree of double refraction becomes, i.e. in case of the same orientation degree of molecules or micelles the tensile strength of films of low polymerization degree is lower than that of high polymerization degree. But the higher the degree of polymerization, the smaller the difference of tensile strength by polymerization degree becomes, and this fact suggests that, in case of still higher polymerization degree, the difference of tensile strength by polymerization degree will become almost nothing.

In case of cellulose films regenerated by alkali saponification of cellulose acetate films, the degree of double refraction is remarkably elevated by saponification. It is clear that hydroxyl groups are regenerated by saponification of cellulose acetate, and the crystallization of the molecules takes place remarkably by the cohesion of hydroxyl groups.

As mentioned above, the mechanism of stretching has been clarified qualitatively by the writer from the measurements of the films or filaments of as many kinds of cellulose derivatives as can be obtained.

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