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A STUDY OF THE EFFECT OF CHAIN LENGTH ($\bar{D}p$) ON THE PRPERTIES OF CELLULOSE TRIACETATE FIBRES

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Four samples of commercial cellulose triacetate were fractionated by both fractional precipitation and gel permeation chromatography.

The mechanical properties of fibres from both triacetate fractions and blends were determined on an Instron tensile tester. A fraction of Dp 76, will not form a coherent filament, fractions of higher Dp showed a rapid improvement of mechanical properties with increase in Dp, , but above 385 further improvement was slight. A fraction with a Dp of 800 was virtually unspinnable. In contract, at any given number average Dp, within the range studied, the properties of the fractions are the same as those of blends, and furthermore those blends which contain fractions of low or very high molecular weight (Dp), are inferior to those which do not. Mechanical properties of triacetate fractions and blends increased with increasing draw ratio but the per cent elongation was greatly reduced.

Electron scanning microscopic studies made on triacetate fibres showed that tensile properties reported here were a function of Dp, rather than the spinning variables.

INTRODUCTION

All synthetic and most natural high polymers are heterogeneous with respect to their chemical structure and/or molecular weight. Fully acetylated cellulose may display dispersity of molecular weight while partially acetylated products may show in addition some chemical structural polydispersity.

Most of the earlier studies on the effect of chain length ($\bar{D}p$) on the mechanical properties of cellulose esters have been carried out on cellulose nitrate [1-6] and secondary acetate [7-11].

There has been substantial agreement amongst most investigators [1, 4, 9, 11-21] that fractionated cellulose derivatives (both cellulose nitrate and secondary acetates) are superior in mechanical properties to blends and unfractionated materials of the same molecular weight. In addition, an increase in the low molecular weight component exerts a harmful effect on the mechanical properties of the blends. Similar conclusions have been reached [22-23, 5-6] for the mechanical properties of films made from fractions and blends of ethyl cellulose.

There is, however, no information in literature about the effect of the chain length ($\bar{D}p$) on the mechanical properties of cellulose triacetate fibres.

The prime object of the present study is to determine the compositional polydispersity of cellulose triacetate and to examine the effect of chain length (molecular weight and molecular distribution on the mechanical properties of the triacetate fibres.

Four samples of commercial cellulose triacetate (supplied by Courtauld's Ltd.), called CTA/S, CTA/M, CTA/3060, and CTA/TG 3323, were fractionated by both fractional precipitation and gel permeation chromatography (GPC), as described in detail by the authors elsewhere[24].

Cellulose triacetate fractions obtained by fractional precipitation were wet spun from dichloromethane as 10% (m/V) solutions using methanol as coagulant. A number of triacetate blends with the same number average molecular weight but with different molecular weight distribution were also wet spun as stated above.

The mechanical properties of fibres produced from both triacetate fractions and blends differing widely in molecular chain length $\bar{D}p$ were determined using an Instron tensile tester. A fraction of $\bar{D}p$ 76 will not form a coherent filament: fractons of higher $\bar{D}p$ showed a rapid impovement in mechanical properties with increase in $\bar{D}p$,

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but above 385 further improvement was slight. Further increase in $\overline{D}p$ caused a sharp deterioration in mechanical properties and a fraction with $\overline{D}p$ 800 was virtually unspinnable. In contrast, at any given number average Dp, within the range studied, the properties of the fractions are the same as those of the blends, and furthermore those blends which contain fractions of very low or very high molecular weight ($\overline{D}p$), are inferior to those which do not. Another notable feature of the blends was the sharp decrease in break elongation as compared to fractions of the same $\overline{D}p$.

The tenacity (in g/denier) for both fractions and blends increased with increasing draw ratio, but the per cent elongation was greatly reduced which is attributed to a higher degree of molecular orientation.

Electron scanning microscopic studies made on the cellulose triacetate fibres revealed that the tensile properties reported in this paper were related to $\overline{D}p$, rather than the spinning variables.

EXPERIMENTAL

Materials

The chemicals and solvents used in this work were all analytical grade materials.

Procedure for Wet Spinning of Cellulose Triacetate Solutions. The design philosophy, constrution and other experimental details of the wet spinning machine used in the present work have already been described in considerable detail elsewhere [25].

A 10% (m/V) solution in dchloromethane for both triacetate fractions and blends was filtered through two layers of gamgee wadding in the purpose built filtration unit. The filtration was carried out at a constant rate, the pressure rising to 60 psi in 10-15 min., and the filtered dope passed directly into the spinning head.

The extrusion took place through a five hole spinneret, each hole being 75 microns in diameter, into a spin bath of 100% mechanol maintained at 12°. After coagulation, the five filaments were taken up at 2.2 m/min., and then passed through a washing bath containing water at 38-42°. The filaments were collected by winding them round specially made bobbins fitted onto the stretch rollers for this purpose. The packaged fibres were dried in an oven at 60° for 30 min. and were then tested on an Instron tensile tester.

Steam Stretching of Triacetate Fibres. When about 20-25 meters of yarn had been collected, as described above, filaments were steam stretched by a factor of 1.5 and 2 respectively. The stretched fibres were packaged, dried and tested as described for undrawn fibres above.

Measurement of Tensile Properties of Cellulose Triacetate Fibre. The tensile properties of all the wet spun triacetate samples, fractions and blends were measured on an Instron TM-M table model tensile tester. The tests were made on 5 cm test length of fibres at a rate extension of 30% per min. The results shown in Tables 1 and 2 are the mean of 10-12 individual tests.

Surface Morhphology and Cross-Sectional Studies on Wet Spun Cellulose Triacetate Fibres by Electron Scanning Microscopy. Surface and cross sectional studies on both undrawn and steam drawn triacetate fibres were made by scanning and transmission electron microscopy. Samples for the scanning electron microscopy were mounted on stubs and coated in vacuo with gold/palladium (Au/Pd) alloy, evaporated from a molydenum strip and were then examined according to the general procedure described by Hearle [26] and Thornton [27].

Samples for transmission electron microscopy were embedded in an araldite mixture, and thin sections prepared using the L.K.B-ultramicrotome. Sections were mounted on copper grids and were then coated with carbon evaporated from an arc prior to examination in the microscope.

The results from both tranmision and scanning electron microscopic studies on wet spun triacetate fibres have been described in the next section of this paper.

RESULTS

Tensile Properties of Wet Spun Cellulose Triacetate Fractions and Blends. The tensile properties of all wet spun triacetate fractions and blends are shown graphically in Fig. 1-4 and in tabular form in Tables 1 and 2 respectively.

Both load of breaking and per cent elongation when plotted against $\overline{D}p$ show a gradual rise in properties up to a $\overline{D}p$ range of 385; above this further improvement with increasing $\overline{D}p$ was slight.

A close correlation between the degree of stretching and initial modulus and tenacity was found (since all these properties are related to the degree of orientation) as shown in Tables 1 and 2).

A rapid drop in the per cent elongation at break may be attributed to a greater degree of orientation. It is evident from Fig. 1 and 2 that both load of breaking and per cent alongation are related to the degree of homogeneity and chain length.

Similar results have been found for triacetate blends as shown in Fig. 4 and Table 2. The presence of a fraction

Table 1. Tensile properties of cellulose triacetate fractions

FRACTION	INTRINSIC VISCOSITY	$\bar{DP}_n$	M_n	LOAD OF BREAKING (g)	% ELONGATION AT BREAK	INITIAL MODULUS (g/den)	TENACITY (g/den)	EXTENT OF STRETCHING (TIMES)	FILAMENT DENIER	REMARKS
CTA/S/UNF	1.78	219	63000	6.07	42.10	35.00	1.35	zero	4.50	Spun fairly
	-do-	-do-	-do-	6.60	6.70	59.20	2.20	1.50	3.00	well (both)
CTA/S/Shoulder Free Material	1.62	320	92000	4.80	42.10	30.00	1.20	zero	4.00	- do -
	-do-	-do-	-do-	5.64	5.94	58.44	2.17	1.50	2.64	- do -
	-do-	-do-	-do-	5.50	5.10	72.56	2.75	2.00	2.00	- do -
CTA/M/1/F2	1.80	384	111090	4.89	60.40	23.45	1.22	zero	4.00	- do -
	-do-	-do-	-do-	5.57	7.10	26.40	1.92	1.50	2.90	- do -
	-do-	-do-	-do-	5.90	5.00	14.36	2.70	2.00	2.20	- do -
CTA/M/1/F1/FA	2.80	793	228375	1.80	30.50	-	-	-	-	Week & Brittle
CTA/M/1/F1/FC	1.40	285	32210	6.00	7.80	142.40	1.20	zero	5.00	Spun fairly
	-do-	-do-	-do-	4.30	4.40	161.60	1.30	1.50	3.30	well (both)
CTA/M/1/F5	1.40	230	66300	3.86	17.00	25.90	0.80	zero	4.80	Week & Brittle
CTA/M/2/F1/FA	2.32	483	139000	4.60	46.00	25.80	1.44	zero	3.20	Hard & Tough
	-do-	-do-	-do-	5.40	6.00	57.60	2.57	1.50	2.10	-do-
	-do-	-do-	-do-	3.80	4.50	78.10	2.71	2.00	1.40	-do-
CTA/M/2/F2	1.84	448	129000	5.00	43.00	28.40	1.40	zero	3.60	Spun very well
	-do-	-do-	-do-	6.84	7.40	55.10	2.80	1.50	2.40	-do-
	-do-	-do-	-do-	11.80	7.90	125.70	5.90	2.00	2.00	-do-
CTA/3060/1/F3	1.82	408	117446	4.20	44.50	22.60	1.20	zero	3.50	Spun very well
	-do-	-do-	-do-	5.40	9.10	71.20	2.30	1.50	2.33	-do-
	-do-	-do-	-do-	4.60	6.20	117.60	2.63	2.00	1.75	-do-
CTA/3060/1/F4	1.02	238	68510	7.24	21.30	25.30	1.51	zero	4.84	Spun as 20% w/w
	-do-	-do-	-do-	6.00	6.40	42.00	1.87	1.50	3.20	-do-
CTA/M/2/F4	0.238	76	22000	-	-	-	-	-	-	Unspinnable
CTA/TG3323/2/F2/FB/Fb	2.44	510	146867	7.20	26.00	8.20	0.60	zero	12.00	Brittle

Table 2. Tensile properties of blends of cellulose triacetate fractions

BLEND	COMPOSITION	WT. % OF EACH FRACTION	$\bar{M}_n$	*$\bar{DP}_n$	LOAD OF BREAKING (g)	% ELONGATION AT BREAK	INITIAL MODULUS (g/den)	TENACITY (g/den)	FILAMENT DENIER	INTRINSIC VISCOSITY	EXTENT OF STRETCHING (TIMES)
a.	CTA/M/1/F2 + CTA/M/1/F1/FA	95 + 5	123000	427	1.70	7.30	90.60	0.60	3.00	1.70	zero
	- do -	-do-	-do-	-do-	1.60	0.88	145.70	0.80	2.00	-do-	1.50
b.	- do -	90 +10	122000	424	2.20	7.82	129.50	1.10	2.00	1.65	zero
c.	CTA/M/2/F3 + CTA/TG3323/2/F2/FB/Fb +	6.66 +40	93312	324	8.00	25.00	57.30	1.25	10.00	1.48	zero
	CTA/TG3323/1/F3	53.30	-do-	-do-	10.23	12.50	182.40	1.55	6.60	-do-	1.50
d.	CTA/M/2/F3 + CTA/TG3323/2/F2/FB/Fb +	20 + 5	86400	300	6.5	18.00	48.10	1.44	4.50	1.52	zero
	CTA/3060/1/F3	+75									
e.	CTA/3060/1/F3 + CTA/M/2/F4	90 +10	87000	302	5.00	30.00	14.00	1.00	5.00	1.38	zero
	- do -	-do-	-do-	-do-	6.50	17.80	61.50	1.96	3.30	-d0-	1.50

* Number Average DP = $\frac{\text{Number Average Molecular Weight}}{\text{Unit Molecular Weight of Triacetate}}$

with Dp 76 had a deleterious effect on the properties, whereas medium and high $\bar{D}p$ fractions had little or no effect on the properties stated above.

Electron Scanning Microscopy of Wet Spun Cellulose Triacetate Fibres. The general surface morphology of the fractions indicated that the wet spun fibres are free of voids and the tensile properties of fractions listed in Table 1 are closely related to $\bar{D}p$ rather than spinning variables.

The shark skin effect of a photomicrograph of the high molecular wight triacetate fibre was attributed to hemicel-

lulose-derivatives [24] present in this fraction.

The cross-sectional photomicrographs of the various triacetate fibres tested were featureless and again no sign of voids or inclusion was observed as mentioned above.

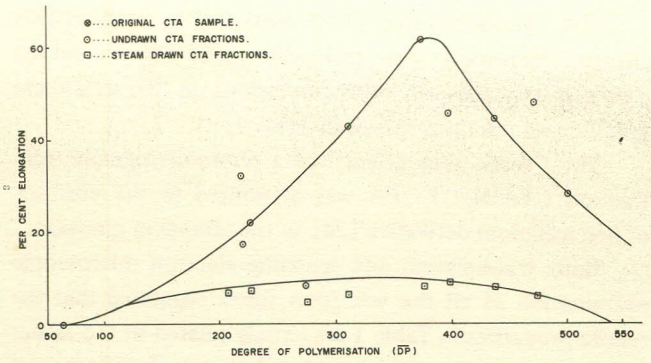

Fig. 1. Per cent elongation of undrawn and steam drawn cellulose triacetate fractions vs $\bar{D}p$.

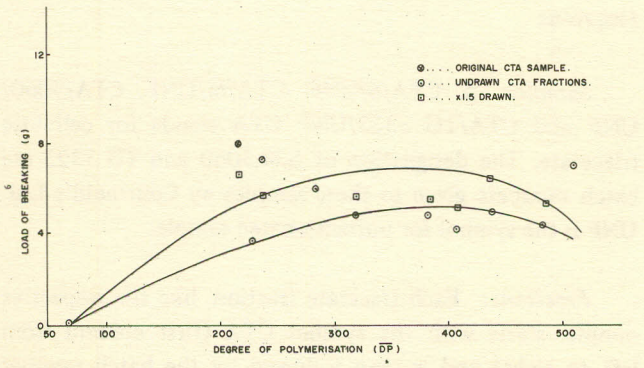

Fig. 2. Load of breaking of undrawn and steam drawn cellulose triacetate fractions vs $\bar{D}p$.

DISCUSSION

Fractions of cellulose triacetate with $\bar{D}p$ up to 800 were obtained by fractional precipitation as described elsewhere [24]. However, work on mechanical properties was limited to fractions with $\bar{D}p$ between 76 and 510. Below this range a coherent filament was not formed and was therefore assigned a zero strength. Fractions above $\bar{D}p$ 510 produced gel-like spinning solutions which resulted in rough surfaced filaments not comparable to those spun from fractions of lower $\bar{D}p$.

These difficulties could have been overcome by the alteration of the concentration of the spinning solutions, but it was found in agreement with Harmons [28] and others [29] that the tensile properties of the filaments were dependent on the concentration of the spinning solution.

Fractions CTA/M/1/F5 and CTA/3060/1/F4 had nearly the same intrinsic viscosity, chain length and number average molecular weight, but when the latter was spun as 20% (W/W) solution in dichloromethane, it produced fibres with superor properties than the former confirming the dependence of concentration on tensile properties.

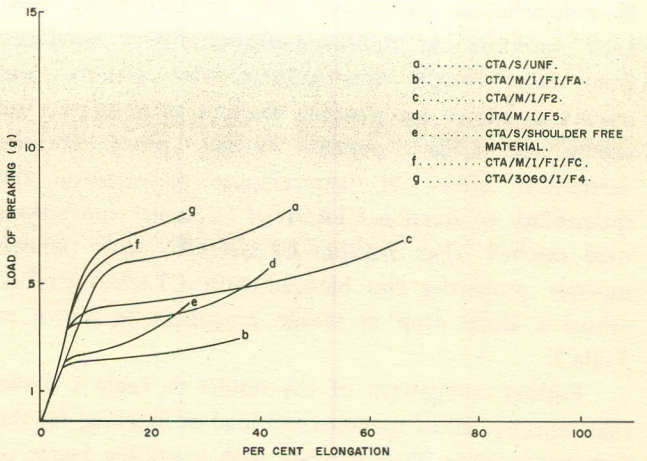

Fig. 3. Tensile properties (Load of breaking vs % elongation) of undrawn cellulose triacetate fraction.

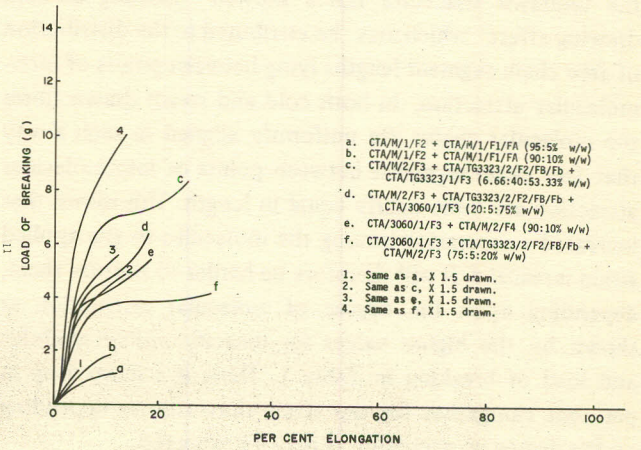

Fig. 4. Tensile properties (load of breaking vs % elongation) of undrawn and steam-drawn blends of cellulose triacetate fractions.

Typical tensile properties for both the undrawn and steam drawn triacetate fractions have been collected together and shown in Table 1. It is evident from these results and also from the plots of per cent elongaton and load of breaking versus $\bar{D}p$ (fig. 1 and 2), load of breaking versus per cent elongation (Fig. 3) for the triacetate fractions in question that tensile properties are dependent on the chain length up to a $\bar{D}p$ of about 320. However, above this $\bar{D}p$, further improvement in properties with increasing chain length was slight until a $\bar{D}p$ of 450 beyond which a sharp drop in properties as a function of $\bar{D}p$ was observed.

In the case of per cent elongation versus $\bar{D}p$ relationship there seems to be a critical $\bar{D}p$, i.e. 400, above which the properties show a rapid decrease as shown in Fig. 1.

All unfractionated cellulose triacetate samples and high molecular weight fractions have been found rich in hemicellulose derivatives [24] as shown by their hazy solutions in dichloromethane. Fibres produced from these sample and fractions were granular and porous as shown by scanning electron microscopy. The results in Table 1 provide further proof of the deleterious effect of hemicellulose derivative on the spinnability of fraction CTA/M/1/F1. Similar conclusions were reached when fraction CTA/M/1/F2 with known superior properties was blended with CTA/M/1/F1/FA, caused a sharp drop in tensile properties as shown in Table 2.

Further comparison of the results in Table 1 shows that tenacity, initial modulus and load of breaking for the various triacetate fibres increase with increasing degree of orientation. The changes in tensile properties have resulted from alteration in microstructure of the fibre. Generally the undrawn triacetate fibres showed "necking or cold drawing effect" which may be attributed to the distribution of free chain segment lengths lying between points of intermolecular attraction. In both cold and steam drawn fibres the molecular chains are uniformly aligned in such a way that free chain segments between points of intermolecular attraction are more nearly equal in length. This means that increased cooperation among the molecules to the applied strain is realized. It will therefore be harder to rupture them, depending upon the degree of molecular orientation as shown by the higher values for tenacity, initial modulus and load of breaking in Table 1. There is a sharp drop in per cent elongation for the steam drawn fibres depending on the degree of stretching as may be expected.

Electron scanning Microscopy of Wet Spun Cellulose Triacetate Fibres. The effect of spinning variables such as dope concentration, extrusion pressure, spinneret hole diameter, composition of the coagulation and wash bath, jet stretch and take up rollers speed have been investigated and described in detail by several workers [30-33] and need not be repeated in this paper.

Attempts were made to keep all these variables constant in the present studies.

Electron scanning microscopic studies were made on triacetate fibres to ensure that the tensile properties reported in Table 1, were related to $\bar{D}p$ rather than the spinning variables stated above.

A comparison of the surface morphology of wet spun triacetate fibres shows a considerable variation in the surface structure of the undrawn fibres, ranging from the granular nature of CTA/M/1/F1/FA to the smooth surface of CTA/M/1/F5.

The cross-section of fibres examined by transmission electron microscopy were featureless and did not reveal the presence of voids or other inclusions in the triacetate samples and fractions shown in Table 1.

The "shark skin effect" of a photomicrograph from fraction CTA/M/1/F1/FA was attributed to the presence of hemicellulose derivative [24] in the sample in question.

Both transmission and scanning electron microscopic examination of all the wet spun fibres suggested that the tensile properties in Table 1 are closely related to $\bar{D}p$ rather than the spinning variables as stated above. The absence of voids, holes and incluions in the photomicrographs of triacetate fibres studied, further confirm these findings.

Nomenclature of Cellulose Triacetate Samples and Fractions.

Samples: Ik CTA/S/UNF, CTA/M/UNF, CTA/3060/UNF and CTA/TG 3323/UNF CTA stands for cellulose triacetate. The designation of S,M,3060 and TG 3323 are batch numbers given to these samples by Courtauld's Ltd. UNF is the symbol for unfractionated sample.

Fractions: Each tracetate fraction, like the respective sample, starts with the symbol CTA (first column from left to right) and is then followed by the batch number (2nd column), fractionation number (3rd column), fraction number (4th column) and sub-fraction number (5th column respectively).

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