

MODIFIED POLYNOSIC FIBRES

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INTRODUCTION

The results to be dealt with in this communication are entirely based on investigations carried out by the authors a few years ago, in a cooperative study regarding the possibilities of modifying Polynosic fibres¹⁻⁵. As a basis for these studies an introductory investigation was carried out concerning the influence of pulp quality, shredding conditions and viscose composition on the manufacture and quality of ordinary Polynosic fibres.

RAYON SULPHITE AND PREHYDROLYSED SULPHATE PULPS

Two principally different types of pulps were investigated, namely: rayon sulphite pulp with alpha-cellulose content of 90.7 per cent and a prehydrolysed sulphate pulp with alpha-cellulose content of 95.7 per cent. From these two types of pulps Polynosic viscoses were manufactured, and the viscose data compared. From this comparison it can be concluded that the viscose from the prehydrolysed sulphate pulp was lower in initial gamma-value and higher in velocity constant of ripening reaction. Accordingly, its ripening time for gamma-value 60 was about 12 h shorter. Further, the prehydrolysed sulphate pulp was lower in viscosity and higher in K_w -values. In this case, therefore, it was found that the prehydrolysed sulphate pulp seemed somewhat inferior to the sulphite pulp with respect to the viscose quality. In the spinning of Polynosic fibres from the two types of pulp, the following conditions were applied:

With a viscose composition of 6 per cent of cellulose and 4 or 5 per cent of alkali, the ripening was carried out at 17°C for 18 h to get viscoses with falling ball viscosities higher than 400 sec, corresponding to gamma-values higher than 60.

SPINNING CONDITIONS

First spinning bath: H_2SO_4 : 26 g/litre
 Na_2SO_4 : 27 g/litre
temperature: 20°C

Second spinning bath: Hot water 80°C (between first and second godet)

Nozzle: No. of holes 200
dia. of hole: 0.07 or 0.06 mm

Spinning speed: 25 m/min

Tension: 2.5 (Second godet speed/first godet speed).

The physical properties of these Polynosic fibres when tested in an Instron apparatus are shown in *Table 1*.

For comparison the physical properties of ordinary rayon staple fibre are also incorporated in *Table 1*, and as is seen the expected high values for the wet modulus characteristics for the Polynosic fibres are well indicated. It was generally found that the hole diameter of the nozzle of 0.06 mm was better than 0.07 mm in spinning behaviour, and the data given in *Table 1* are all for the 0.06 mm nozzle. It may further be mentioned that in viscosity dependence on alkali content the viscose prepared from sulphate pulp showed less dependence than the viscose from sulphite pulp. This may be due to differences in the chain length distribution of the pulps. On the whole the influence of pulp type and alkali content in the viscose on spinning behaviour and physical properties was not very significant, as will be seen from *Table 1*.

Table 1. The influence of pulp quality, alkali content in viscose and hole diameter of nozzle upon physical properties of Polynosic fibres

Pulp	Viscose viscosity (sec)	Denier	Strength (g/den.)		Elongation (%)		Wet modulus (g/den.)	
			Dry	Wet	Dry	Wet	5%	Rupture
Sulphite pulp	534	1.71	3.52	2.32	11.3	13.5	11.7	17.2
	847	1.71	2.98	2.28	11.6	14.2	13.7	16.1
Sulphate pulp	422	1.70	2.52	2.40	10.1	13.7	12.9	17.5
	540	1.70	3.29	2.37	10.9	13.9	14.1	17.1
Ordinary rayon staple fibre		1.5	2.3	1.2	20	25	5.3	4.8

MIXED POLYNOSIC-CELLULOSE ETHER FIBRES

In order to investigate the possibilities of modifying the wet modulus and accessibility of Polynosic fibres by means of mixed spinning with cellulose ethers, a series of commercial cellulose ethers was used in this work as indicated in *Table 2*.

Table 2. Degree of substitution or molar substitution of cellulose ethers

Cellulose ether	Degree of substitution or Molar substitution					Total
	Hydroxyethyl	Methoxy	Ethoxy	Carboxymethyl	Hydroxypropyl	
Hydroxyethyl cellulose*	1.32	—	—	—	—	1.32
Hydroxyethyl cellulose†	0.24	—	—	—	—	0.24
Methoxy cellulose*	—	1.62	—	—	—	1.62
Ethoxy cellulose†	—	—	0.63	—	—	0.63
Carboxymethyl cellulose*	—	—	—	0.71	—	0.71
Methoxyhydroxypropyl cellulose*	—	1.22	—	—	0.20	1.42
Ethoxyhydroxyethyl cellulose*	0.61	—	0.80	—	—	1.41

* Normal degree of substitution (water soluble)

† Low degree of substitution (alkali soluble)

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Table 3. Filterability and viscosity dependence on temperature for cellulose ethers in alkaline solutions

<i>Cellulose ether</i>	<i>Conc.</i> (%)	<i>Falling ball viscosity (sec)</i>				$K_w \times 10^{-2}$
		<i>Temperature</i>				
		20°C	30°C	40°C	50°C	
Hydroxyethyl cellulose*	3	1.1	0.7	0.4	0.3	6
	4	2.8	1.8	1.3	1.0	12
	5	6.4	4.3	3.0	2.0	18
Hydroxyethyl cellulose†	6	49.7	30.7	21.8	16.5	432
	3	0.9	∞	—	—	476
	4	5.1	∞	—	—	5714
Methoxy cellulose*	5	18.5	∞	—	—	8000
	3	8.7	6.0	9.0	∞	66
	4	30.2	22.3	136.0	∞	84
Ethoxy cellulose†	5	98.0	74.0	∞	—	277
	3	3.5	2.4	1.6	1.4	559
	4	12.4	8.0	6.0	4.0	881
Carboxymethyl cellulose*	5	35.0	22.5	15.5	10.6	1220
	3	1.4	1.5	∞	—	103
	4	4.0	4.4	∞	—	208
Methoxyhydroxypropyl cellulose*	5	11.6	33.0	∞	—	339
	3	2.5	1.8	1.5	11.3	271
	4	6.9	4.9	5.0	41.8	388
Ethoxyhydroxyethyl cellulose*	5	22.7	17.6	67.8	∞	639

* Normal degree of substitution (water soluble)

† Low degree of substitution (alkali soluble)

∞: coagulation

In order to be used for mixing with Polynosic viscose, these cellulose ethers in alkaline solutions were studied with respect to their filterability and viscosity dependence on temperature. The results are given in *Table 3*, and it should be mentioned that the alkali concentration was kept constant at 6 per cent, and as will be seen, the cellulose ether concentration was changed, namely between 3, 4 and 5 per cent. One exception is the low substituted hydroxyethyl cellulose, where 6 per cent cellulose ether concentration was applied, and an alkali concentration of 8 per cent.

It may be stated that comparing with viscose in general, these cellulose ethers in alkaline solutions have very high K_w -values. Normally substituted hydroxyethyl cellulose solution was the one with the lowest K_w -value. Thus to judge from these experiments on the whole it seems absolutely necessary to filter these cellulose ether solutions before mixing them with Polynosic viscose because of their very high K_w -values.

From the data in *Table 3* it is further clearly understood that cellulose ethers containing hydrophobic substituted groups are not very well adaptable for a mixing with Polynosic viscose.

SPINNING BEHAVIOUR OF MIXED VISCOSES

As is further seen from *Table 3*, mixtures of methoxy cellulose with normal degree of substitution have extremely high K_w -values, and in addition a lot of air bubbles were found in the viscose. Its spinning seemed therefore to be impossible, and this cellulose ether was therefore rejected, whereas the other six samples were used for mixed spinning with Polynosic viscose.

The spinning conditions were all as mentioned above, and the results from these experiments are found in *Table 4*. The mixing ratio of cellulose ether to cellulose was in all cases 1 part to 10 parts.

From these experiments it may be concluded that mixtures with hydroxyethyl cellulose showed good spinning behaviour especially in the case of the low substituted one. Mixtures with low substituted ethoxy cellulose or ethoxyhydroxyethyl cellulose with normal degree of substitution were not very good in spinning behaviour. Mixtures with methoxyhydroxypropyl cellulose were impossible to spin due to the amount of air bubbles in the mixed viscose. Mixtures with carboxymethyl cellulose having normal degree of substitution showed rather good spinning behaviour, but a few broken filaments were observed in the second spinning bath under stretching.

In physical properties mixtures of hydroxyethyl cellulose had the highest wet modulus values.

Generally it may be concluded that mixed Polynosic fibres with hydroxyethyl cellulose or carboxymethyl cellulose have possibilities of modifying these fibres in many ways. As hydroxyethyl cellulose seemed to show the most interesting results for our purpose, especially the low substituted one, a more thorough investigation was carried out on the adaptability of hydroxyethyl cellulose for mixed spinning with Polynosic viscose.

Table 4. Physical properties of mixed Polynosic fibres
(The data recorded are mean values of spinning results with 0.06 and 0.07 nozzles)

<i>Cellulose ether</i>	<i>Denier</i>	<i>Strength</i> (g/den.)		<i>Elongation</i> (%)		<i>Wet modulus</i> (g/den.)	
		<i>Dry</i>	<i>Wet</i>	<i>Dry</i>	<i>Wet</i>	<i>5%</i>	<i>Rupture</i>
Hydroxyethyl cellulose*	1.75	3.43	2.16	11.9	11.2	16.6	19.2
Hydroxyethyl cellulose†	1.75	4.01	2.41	11.8	11.5	19.0	21.4
Ethoxy cellulose†	1.75	2.97	2.20	11.0	12.4	12.4	17.9
Carboxymethyl cellulose*	1.73	2.70	2.26	8.9	12.3	12.8	18.5
Ethoxyhydroxyethyl cellulose*	1.76	3.35	2.26	11.2	12.8	11.2	17.8
Methoxyhydroxypropyl cellulose*		Spinning was impossible					

* Normal degree of substitution (water soluble)

† Low degree of substitution (alkali soluble)

PREPARATION OF HYDROXYETHYL CELLULOSE

In the preparation of hydroxyethyl cellulose the liquid phase etherification procedure was applied. Alkali cellulose prepared by conventional procedure was etherified by admixture of ethylene oxide and acetone in the shredder (equipped with condenser). Then the product was neutralized by methyl acetate refined by a mixture of acetone-methanol (1 part/1 part by volume) and dried in a vacuum drier. These hydroxyethyl celluloses were tested with regard to molar substitution, viscosity of their alkaline solutions (cellulose ether 5 per cent, alkali 5 per cent), and the filterability of these solutions. The results show that the molar substitution increased as more ethylene oxide was used, and the etherification temperature was raised. On the other side the viscosity and K_w -values of the alkaline solution decreased with increasing degree of molar substitution. A series of experiments was

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then carried out in order to investigate the influence of the alkali concentration in the mercerization step. The following alkali concentrations were selected: 18, 25 and 30 per cent as sodium hydroxide g/100 g. The etherification conditions were as follows:

Ethylene oxide:	42 ml
Acetone:	70 ml
Temperature:	30°C
Time:	4 h
Amount of alkali cellulose:	150 g

It was found that it was not necessary to use alkali concentrations above 18 per cent in the mercerization stage, because the molar substitution did not increase beyond this level, and the cellulose was degraded when higher concentrations of alkali were applied. The filterability was in all cases found to be satisfactory compared with the filterability of the commercial hydroxyethyl celluloses used in the previous experiments.

SOME CHARACTERISTICS OF MIXED POLYNOSIC FIBRES

Medium substituted hydroxyethyl celluloses of molar substitution 0.90 and 0.49, prepared as described above, were used in mixed spinning with Polynosic viscose at a ratio cellulose ether/cellulose: 1 part/10 parts. The procedure of viscose preparation and spinning was the same as described above. Ordinary Polynosic fibres were spun at the same time for comparison. The physical properties of the spun fibres are shown in *Table 5*.

Table 5. Physical properties of mixed Polynosic fibres with medium substituted hydroxyethyl cellulose

<i>Sample</i>		<i>Denier</i>	<i>Strength (g/den.)</i>		<i>Elongation (%)</i>		<i>Wet modulus (g/den.)</i>		<i>Loop strength (g/den.)</i>
<i>Polynosic fibre</i>	<i>Molar substitution of hydroxyethyl cellulose</i>		<i>Dry</i>	<i>Wet</i>	<i>Dry</i>	<i>Wet</i>	<i>5%</i>	<i>Rupture</i>	
Mixed	0.90	1.80	3.10	2.09	10.0	10.3	13.2	20.3	0.73
Mixed	0.49	1.80	3.31	2.39	11.6	10.7	13.0	22.3	0.70
Ordinary		1.66	2.82	2.23	8.9	12.2	12.8	18.3	0.72

As is seen from *Table 5*, the mixed Polynosic fibres with medium substituted hydroxyethyl cellulose did not show higher values in 5 per cent wet modulus than ordinary Polynosic fibres, but they were higher in wet modulus at rupture. In spinning behaviour mixtures of medium substituted hydroxyethyl cellulose were very stable, especially the one with molar substitution 0.49.

A picture of the relationship between molar substitution of hydroxyethyl cellulose and wet modulus of mixed Polynosic fibres, is given in *Table 6*. The results seem to indicate that one can generally conclude that a low degree of substitution in the hydroxyethyl cellulose is best suited for making modified Polynosic fibres, having higher wet modulus characteristics.

Finally it should be mentioned that fibrous acetylation of mixed Polynosic fibres with hydroxyethyl cellulose has been performed in order to get high wet modulus acetate fibre. Further, the change of the fine structure in the modification of Polynosic fibre with low substituted hydroxyethyl cellulose also seems to give the most interesting results.

Table 6. The relation between molar substitution of hydroxyethyl cellulose and the wet modulus of mixed Polynosic fibre

Sample		Wet modulus (g/den.)	
Polynosic fibre	Molar substitution of hydroxyethyl cellulose	5%	Rupture
Mixed	1.32	16.6	19.2
Mixed	0.90	13.2	20.3
Mixed	0.49	13.0	22.3
Mixed	0.24	19.0	21.4
Ordinary	—	12.8	18.3

References

- ¹ T. Mikami and Ø. Ellefsen. *Norsk Skogind.* **16**, 563 (1962).
- ² T. Mikami and Ø. Ellefsen. *Norsk Skogind.* **17**, 57 (1963).
- ³ T. Mikami and Ø. Ellefsen. *Norsk Skogind.* **17**, 104 (1963).
- ⁴ T. Mikami and Ø. Ellefsen. *Norsk Skogind.* **17**, 151 (1963).
- ⁵ T. Mikami and Ø. Ellefsen. *Norsk Skogind.* **17**, 232 (1963).