

"SOME PHYSICAL AND CHEMICAL PROPERTIES OF THE CELLULOSIC FIBRES PREPARED FROM EGYPTIAN LINEN"

A thesis

Submitted in Partial Fulfilment of the requirements of the M.Sc. degree in Chemistry

541-341 M. S

presented by:-

Mohamed Soliman AbdEl-Salam B.Sc. (very good with honour degree) 50875

Supervised by:-

Prof. Dr. Sald Th. AbdEl-Rahim Prof. of Physical Chemistry Faculty of Science Ain Shams University Prof. Dr. Mohammed H. Fadi Prof. of Cellulose Chemistry National Research Centre Dokki

Prof. Dr. Magdi Z. Sefain Prof. of Cellulose Chemistry

> N.R.C Dokki

Department of Chemistry
Faculty of Science
Ain Shams University
Cairo - Egypt
1994 -

"Some physical and chemical properties of the cellulosic fibres prepared from Egyptian linen"

THESIS ADVISORS

THESIS APPROVED

Prof. Dr. Said Th. AbdEl-Rahim

Prof. Dr. Mohammed H. Fadl

Prof. Dr. Magdi Z. Sefain

Head of Chemistry Department

Prof. Dr. A.F. M. Fahmy

A.F.M. Fahmy



Acknowledgement

The author wishes to express his thanks to Prof. Dr. S. Th. Abdel Rahim, Prof. of Physical Chemistry, Faculty of Science, Ain Shams University for his help and guidance.

Special and sincere thanks are due to Prof. Dr. Mohamed H. Fadl, and Prof. Dr. Magdi Z. Sefain, Cellulose and Paper Department, National Research Centre, for their supervision suggestion, discussion and valuable criticism throughout the work.

Appreciation is also devoted to Dr. Nahla A. R. El-Wakil, Researcher, Cellulose and Paper Department, National Research Centre, for her valuable help offered during the discussion and preparation of the present work.

Thanks are also to all the technical staff in Cellulose and Paper Department for their great effort in manipulation of lab. instruments.

Grateful acknowledgement is expressed for the facilities rendered by the National Research Centre, Egypt, which made this work possible.



2.3.3 Sodium chlorite/potassium permanganate mixture	22
2.4 Chemical analysis of the investigated samples	23
2.4.1 Hollocellulose estimation	23
2.4.2 Alpha-Cellulose estimation	24
2.4.3 Lignin estimation	24
2.4.4 Pentosan estimation	26
2.4.5 Ash content estimation	28
2.4.6 Water retention value estimation	28
2.5 Xanthation of cellulosic fibres prepared from linen	29
2.6 Acetylation of the cellulosic fibres prepared from	
linen	30
2.6.1 Activation	31
2.6.2 Acetylation	31
2.6.3 Stabilization	32
2.6.4 Combined acetic acid estimation	32
2.7 Thermal behaviour of chemically treated linen fibres	33
2.8 X-Ray investigation	33
2.9 Infra-Red spectra	33
III. RESULTS AND DISCUSSION:	
3.1 Chemical constitution and W.R.V of the untreated and	
alkali treated fibres	34
3.1.1 The lignin content	34
3.1.2 The hemicellulose content	34
3.1.3 The α -cellulose content	38
3.1.4 The ash content	38

	3.1.5 The water retention values	38
3.2	Rate of delignification of native sample treated with	
	5% sodium hydroxide at 120 °C for different periods	42
3.3	Comparison between chemical constituents and W.R.V of	
	different bleached linen fibres	42
	3.3.1 The lignin content	42
	3.3.2 The hemicellulose content	46
	3.3.3 The α -cellulose content	46
	3.3.4 The ash content	49
	3.3.5 The water retention values	49
	3.3.6 Discussion	49
3.4	Reactivity of the chemically treated samples	54
	3.4.1 Rate of xanthation	54
	3.4.1.1 Comparison between the reactivity	
	of the differently bleached cellul-	
	osic fibres prepared from linen	65
	3.4.1.2 Kinetic investigation on the	
	reactivity of the cellulosic	
	fibres prepared from linen	
	towards xanthation	67
	3.4.2 Rate of Acetylation	74
3.5	Thermal behaviour of the cellulosic fibres prepared	
	from linen	80
	3.5.1 Thermal gravimetric analysis.	80

3.5.1.1 Kinetic investigation of the
degradation processes 87
3.5.1.2 Changes occurred in the activation
energy values 92
3.5.2 Differential thermal analysis of the
investigated samples 92
3.6 X-Ray analysis of the investigated samples 94
3.7 Infra-Red spectra of the investigated samples 99
IV REFERENCES 103
ARABIC SUMMARY

SUMMARY

Summary

In the present work, the linen fibres were chosen as a non conventional source of the cellulosic fibres used for different reactions. The linen fibres were treated with different concentrations of sodium hydroxide at different temperatures followed by treatments with various bleaching agents, i.e, sodium chlorite, sodium hypochlorite and sodium chlorite/potassium permanganate mixture.

The obtained samples were investigated for their reactivities towards xanthation and acetylation, thermal behaviour and the structure has been investigated using X-ray and I.R techniques.

It was found that, treatment with sodium hydroxide, either at low or high temperatures, has a limited effect on the lignin, hemicellulose and Q-cellulose contents. Different bleaching agents differently affected the lignin content, and other chemical constituents which may be related to either the effect of alkali pretreatment or to the effect of the bleaching agents used. It is also found that, although alkali pretreatment at 120°C has no significant effect on the chemical constituents of the samples, yet, bleaching of these samples affected to a great extent their chemical constituents.

The reactivity of the samples, towards xanthation and acetylation were investigated, cotton linter was taken as a reference due to similarities in its supermolecular structure and its utilization with those of linen. It was found that samples treated with sodium chlorite/potassium permanganate mixture are more reactive towards xanthation than those treated with the other reagents; whereas reactivity towards acetylation was found to be poor. This was assumed on the basis of the increased diffusion rate of the positively charged reactants into the activated cellulosic fibres i.e, negatively charged fibres. The kinetic of the xanthation reaction was investigated and it was found that, it follows a first order rate equation.

Thermal stability of some selected samples were investigated using thermogravimetric analysis and differential thermal analysis techniques. Studying the kinetic of weight loss in the main degradation step shows that, it follows a first order rate equation and turns complicated at the end of this stage. The activation energy values for degradation process were evaluated and it was evident that, the stability of the samples towards degradation was decreased by using sodium chlorite/potassium permanganate mixture compared with the stability of the untreated linen fibres. It was also found that, thermal degradation of the samples proceeds via two exothermic processes; except those bleached with sodium chlorite/potassium permanganate mixture which were found to proceed via three

F.,

exothermic reactions and this was discussed on the possible production of some thermally stable fragments, which degraded at relatively high temperature.

X-ray diffraction pattern showed that, the chemical treatments increases the crystallite size and this increase is related to the alkali pretreatment temperature rather than the type of the chemicals used. The d-spacing for 002 equatorial reflection was found to be unaffected.

I.R investigation of the samples showed that, the increased reactivity of some samples may be related to the increased number of free hydroxyl groups (non bonded). The degree of order, represented as crystallinity index, was estimated from the I.R absorption bands as the ratio of $1429 \, \mathrm{cm}^{-1}/893 \, \mathrm{cm}^{-1}$, for the above samples and it was found that the slight increase in their values may be ascribed to the possible reordering of the chains, or may be related to the degradation of the disordered regions (removal of non-ordered lignin) which enhance the degree of order.

L INTRODUCTION

INTRODUCTION

In contrast to Cotton, Linen is found as bundles in the stem of the plant which have the scientific name "Linium usitatissimum". It is classified with other fibres such as Ramie, Jute etc., as a bast fibre 1

The word "flax" is also used to designate the linen fibres, which is derived from "fleax" Anglo-Saxon, and "flachs" old high German. Although, the word "fleax" is understood in most countries, the word "Linen" is more widely used both to designate the plant as well as the fibres. In English-speaking countries, "Linen" is generally used to designate the yarns and fabrics made from flax fibres 2

1.1 Occurrence and external structure of the linen:

The plant requires high moisture and cool weather during the growing season. Although relatively little linen fibres are grown in U.S.A, the Willamette Valley in Oregon, and the Puget Sound region in Washington seem to have the most desirable conditions. Seed linen is grown largely in North and South Dekota, Western Minnesota and Eastern Montana, which produced about 95% of all linen grown in the U.S.A; more recently, it has been introduced as a cash crop in California. In Europe, in Lorentz years, Russia was by far the greatest cultivator of

linen, but no accurate statistics are available of the amount grown in recent years. Other European countries, in order of importance in the cultivation of linen, are Czechoslovakia, France, Germany, Italy, Belgium and Ireland. Ireland and Belgium are the most noted as producers of the linen³

In Egypt, during the eleven years (1977-1987), production of linen-straw was varied from 156,000 tons in 1977 to 200,000 tons in 1980/1981 and then decreased to 96.000 tons in 1987/1988. This variation in production is due to variation in the area cultivated with linen, where 58,500 Fed. were cultivated in 1977 in contrast to 68,000 Fed in 1980 and 35,000 Fed in 1988. This variation in the production of linen straw had a negative impact on the fibre production and showed a production decrease from 20.200 tons in 1980 to 11,700 tons in 1987. This has been reflected on the exportation market, where linen fibres exportation has been declined during this period from 16,300 tons in 1980 to 7,800 tons in 1987. It is claimed that for the year 2000, 70,000 Fed. will be cultivated with linen to produce 225,000 tons linen straw equivalent to 34,000 tons fibres from which 15,000 tons can be exported to foreign markets4. But, neither country produces sufficient linen to satisfy the demands of the users and much of the fibres has to be imported.