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Matsuo Hirami[a]
[a] Unitika Ltd., Kyoto, Japan

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NEW DEVELOPMENTS IN THE RAYON INDUSTRY

MATSUO HIRAMI

Unitika Ltd.
Uji, Kyoto 611, Japan

INTRODUCTION

In August 1988 the International Symposium of Macromolecules (MACRO 88) was held at the International Conference Hall located in the northeastern part of Kyoto. At the same time, at the National Museum in the southeastern part of the city, an exhibition of Treasures of Ancient Egypt, including rolls of papyrus (the origin of paper) was displayed. At the symposium, Prof. Nishijima [1], President of Kyoto University, gave an address in which he stated " . . . I feel there is something more than mere coincidence that both this symposium of MACRO 88 and the exhibition of Egyptian Art and Technology are held at the same time in the North and South of Kyoto. The civilization of 5000 years ago meets most recent developments of integrated science and technology as MACRO 88. It is the accession over the span of millennia."

Indeed, cellulose used in paper and clothing is the most important among the polymer materials related to the culture and technology of human beings in this 5000 years. Rayon technology played a leading role in the era of man-made fibers which began at the end of the previous century. New developments in rayon technology give us hope for progress in the next generation.

HISTORY OF RAYON INDUSTRY

It may be useful to mention briefly the history of the rayon industry, especially in Japan [2]. Modernization of the cotton industry as realized by major developments and enhanced productivity of spinning and weaving machines, played an important role in the Industrial Revolution. This occurred mainly in England between the end of 17th century and the beginning of 18th century.

In the 19th century the technology of regenerated cellulose fiber based on chemical dissolution and spinning of dope solution was initiated. Various technologies of rayon fibers were developed: the invention of cellulose nitrate by C. F. Schonbein in 1845, the dissolution of cellulose in cuprammonium discovered by E. Schweizer in 1857, the invention of cellulose triacetate by P. Schutzenberger in 1869, the first man-made fiber of the viscose process by H. deChardonnet in 1884, and the invention of the viscose process by C. F. Cross and E. J. Bevan in 1892.

The advantage of the viscose process for industrial production became recognized in the 1910s among several candidates of the processes of regenerated cellulose fibers. Later, the production of viscose rayon was increased in Europe and elsewhere. After World War I, the United States became the top producer.

One century later than in the UK, the fiber industry played an important role in Japanese industry as it developed after the Meiji Restoration (1868). The first modernized spinning plant, based on the latest technology of England, was created in 1882. The company's name was Osaka Boseki, now Toyobo, and it was the first joint-stock corporation in Japan. Many companies followed. The Japanese cotton industry developed remarkably, and it had the highest exportation of cotton fabrics in the world before World War II.

In 1913, Prof. Hata of Yonezawa Polytechnic, now Yamagata University, succeeded in the first spinning test of viscose rayon yarn in Japan. Using this technology, the first production plant for viscose rayon of Teijin was started in Yonezawa city. Several companies followed. These companies can be categorized into three types: 1) those started through the support of trading companies, Teijin and Toray; 2) as a branch business of a chemical company, Asahi Chemical; and 3) as a new fiber business of spinning companies, Toyobo, Kanebo, and Unitika. The Japanese viscose rayon industry had grown remarkably and reached a peak production of about 150,000 tons in 1937. Later, the Japanese fiber industry started the production of viscose rayon staple, which was mainly developed in Germany, and reached a peak production of about 140,000 tons in 1938.

During World War II the production of rayon in Japan was reduced, and the industry was almost destroyed by the end of the war. However, the rayon industry recovered after the war, and production reached 100,000 ton/y of filament and 350,000 ton/y of staple.

AS A GUIDING TECHNOLOGY FOR THE SYNTHETIC FIBER INDUSTRY

The invention of nylon by Carothers of DuPont in 1938 was the dawn of the synthetic fiber era. After World War II, Toray (1951) and later Unitika (1955) begun to manufacture nylon. Polyester (PET) appeared after nylon, and became the leading synthetic fiber. The technology of the Japanese fiber industry contributed to the productivity and quality of synthetic fibers.

I would like to emphasize that the technologies of synthetic fibers were developed by learning from rayon technology in process engineering, quality control systems, and product design based on the structure–properties relationships.

The melt spinning process was the productivity breakthrough. The take-up speed of the melt spinning process was initially over 10 m/min. When the two-step process was established, where fiber was taken-up over 100 m/min and drawn at a

TABLE 1. Yarn Properties of PET and Rayon[a]

	PET-I	PET-II	Rayon
Den./fil.	1500/192	1500/252	1650/1100
Breaking strength (kg)	14.41	12.28	10.10
Elongation (%)	15.8	13.7	8.7
Tenacity (g/d)	9.52	8.15	6.00
Modulus (g/d)	99	88	142
Shrinkage at 180°C (%)	13.0	6.1	2.0

[a]PET-I: conventional PET tire yarn. PET-II: rayon-like PET tire yarn.

ratio of about 4. The partially oriented yarn (POY) process was developed later. After the 1970s the trend was to high speed spinning to produce fully oriented yarn (FOY), and nowadays process technology with a take-up speed of 6000 m/min has been established. The use of such high speed spinning technology is the primary reason for the economic advantage that established the synthetic fiber era.

Synthetic fibers, mainly nylon and PET, have grown in both their industrial application and textile apparel usage. In the latter application, the Japanese fiber industry has made a remarkable contribution with the development of a series of high level fashion-oriented fabrics. "Shin-Gousen." This success was accomplished by an interface among oriental culture, sensitivity, the development of microfiber technology, and sophisticated after-treatment. Viscose rayon has been reevaluated as a unique material with good fit to the human body and a comfortable feel, and applied partially to Shin-Gousen. Unitika lately developed a rayon-PET commingled yarn as one of the Orquesta series.

Viscose rayon has superior properties for industrial application. High tenacity rayon yarn is used in the radial tires of Michelin. In this field, high modulus and low shrinkage (i.e., the good dimensional stability of rayon) were utilized for the design of tires with superior handling and comfortableness. Tables 1 and 2 summarize the properties of conventional and rayon-like PET yarn.

TABLE 2. Cord Properties of PET and Rayon[a]

	PET-I	PET II	Rayon
Cord construction	1500D/2	1500D/2	1650D/2
Twist (tpm)	400 × 400	400 × 400	470 × 470
Breaking strength (kg)	23.05	23.32	15.60
Elongation at 6.75 kg (%)	3.8	3.7	3.2
Elongation at break (%)	16.6	12.6	9.9
Tenacity (g/d)	6.88	6.65	4.50
Modulus (g/d)	61	59	80
Shrinkage at 150°C (%)	6.3	4.2	1.0

[a]PET-I: conventional PET tire yarn. PET-II: rayon-like PET tire yarn.

LYOCELL FIBER

Viscose rayon is an excellent regenerated cellulose fiber material. However, its production problems include a complicated process of dissolution and coagulation, and the generation of by-products. According to Tribak, the dissolving mechanism of cellulose in a solvent is classified into four types as listed in Table 3. Rayon and cellulose acetate are categorized as type I, and cuprammonium cellulose belongs to type II. Good solvents for types III and IV, which are simpler processes, are desired. However, it has been difficult to find a good solvent because strong solvents are usually accompanied by strong disintegration and hence there is a large molecular weight drop. After a number of investigations, *N*-methylmorpholine *N*-oxide (NMMO) was developed. The solvation mechanism is probably the cleavage of intermolecular bonds in cellulose as a result of the interaction between the highly polar NO of NMMO and the OH of cellulose. This was first studied by Johnson at Eastman Kodak and later at Akzo. Finally, Coutaulds [3] in the UK succeeded in commercializing it under the trademark of Tencel. Scheme 1 shows the process for the production of Tencel. The cellulose is dissolved in NMMO, the solution is filtered and spun into a dilute aqueous solution of amine oxide to produce Tencel. The air-gap method is employed rather than the conventional wet spinning process.

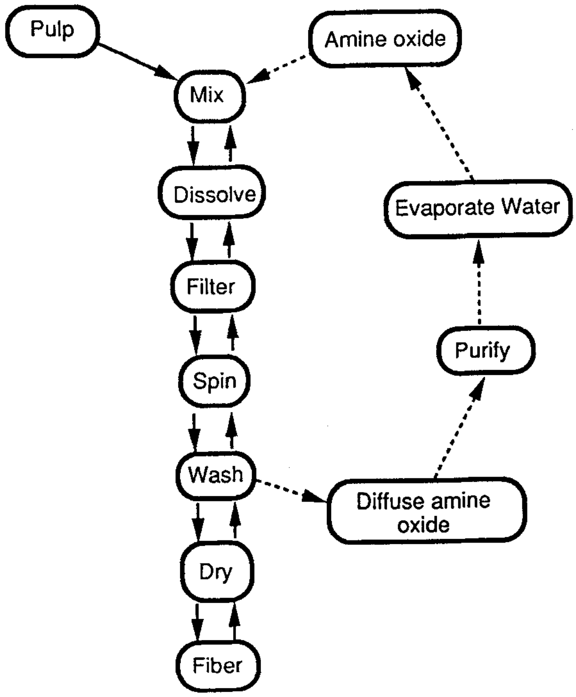
Coutaulds constructed a semicommercial plant in Grimsk, England, in 1988 and started a commercial plant in Mobile, Alabama, USA, in 1992. Marketing research and development are carried out in the United States, for industrial usage and in Japan for textile apparel.

Table 4 and Fig. 1 show the properties of Tencel compared to conventional materials. Among its many superior properties, the high ratio of wet strength against dry strength is significant. The cross section is circular, and the fiber surface is smooth and has serrated crimps. The name Lyocell for the cellulose fiber produced by solvent spinning was given by BISFA. The commercialization of Lyocell was developed by Lenzing, Austria. Lyocell is only produced as a staple fiber so far. In November 1994 Courtaulds, UK and Akzo Nobel, Netherlands announced the start of a joint research project of filament yarn of Lyocell. It is believed that

TABLE 3. Classification of dissolving mode[a]

	Dissolving scheme	Application
I	A solvent which dissolves cellulose by forming a cellulose derivative	Viscose rayon Cellulose acetate fiber
II	A solvent which dissolves cellulose by forming a complex with cellulose	Cellulose fiber made from cuprammonium
III	A solvent which dissolves cellulose as acid	
IV	A solvent which dissolves cellulose as amine	Lyocell Tencel

[a]A. F. Turbak et al., *ACS Symp. Ser., 58*, preprint p. 12 (1977); A. F. Turbak, *Tappi J., 67*(1), 94 (1984).



SCHEME 1. The Tencel production process.

TABLE 4. Fiber Properties of Tencel[a]

	Tencel	Viscose	Cotton
Linear density (dtex)	1.5	1.7	
Tenacity (cN/tex)	38–42	22–26	20–24
Elongation (%)	14–16	20–25	7–9
Wet tenacity (cN/tex)	34–38	10–15	26–30
Wet elongation (%)	16–18	25–30	12–14
Tenacity at 10% (cN/tex)	35	16	
Wet modulus at 5% (cN/tex)	27	5	10
Moisture regain (%)	11.5	13	8
Water imbibition (%)	65	90	50

[a]Source: Courtaulds Technical Information.

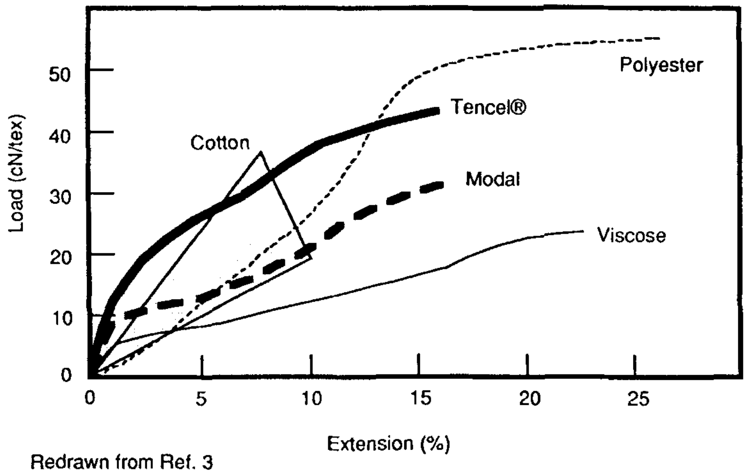


FIG. 1. Stress-strain properties: Tencel compared with other fiber types.

Lyocell has potential application for cellulose materials of staple fibers, filament yarn, nonwoven fabrics, film, etc.

APPLICATIONS

Table 5 summarizes the types, materials, and applications of cellulose and its derivatives [4].

Cellulose-based membranes provide excellent separation ability, ranging from a few nanometers to a few micrometers. Membranes for dialyzers are a successful application. Various novel applications are under research.

Nonwoven fabrics of cellulose have been applied to domestic, hygienic, and industrial usage. For example, spunlace of cotton commercialized in Japan has obtained a high reputation. The application of nonwoven fabrics of Lyocell by spunlace is under development.

Wrinkle-free (non-iron) shirts of cotton prepared by vapor phase treatment have been successfully commercialized in Japan. The enzymatic reduction of cellulose fabrics is now being studied.

BIODEGRADABILITY OF RAYON

The characteristics of good biodegradability of cellulose-like rayon are noteworthy. Figures 2 and 3 show published and unpublished data measurements from our laboratory. This significantly superior property of synthetic fibers should be emphasized when we consider environmental protection.

TABLE 5. Cellulose and Its Derivatives [4]

Type	Material	Application
Celluloses	Cotton, linen	Fiber, nonwoven fabrics
	Powdered cellulose	Filter
	Microcrystal cellulose	Medical, chromatography
	Microfibril cellulose	Foods, cosmetics
Regenerated celluloses	Viscose	Fiber, tire yarn
	Benberg	Fiber, dialyzer
	Tencel	Fiber
	Spherical cellulose	Chromatograhy, cosmetics
	Cellophane	Food-wrapping film
	Sponge, nonwoven fabrics	Domestic goods
Esters	Cellulose acetate	Fiber, film
	Cellulose nitrate	Paint, gunpowder
	Cellulose acetate phthalate	Medical (masking)
	Cellulose acetate butylate	Plastics
Ethers	Methylcellulose	Cement mixture, sizing agent
	Ethylcellulose	Lacquer, paint
	Hydroxyethylcellulose (HEC)	Paint, latex
	Hydroxypropylcellulose (HPC)	Medical (adhesive), cosmetic
	Carboxymethylcellulose (CMC)	Foods, binder, adhesive
Etheresters	Various	Medical (masking)

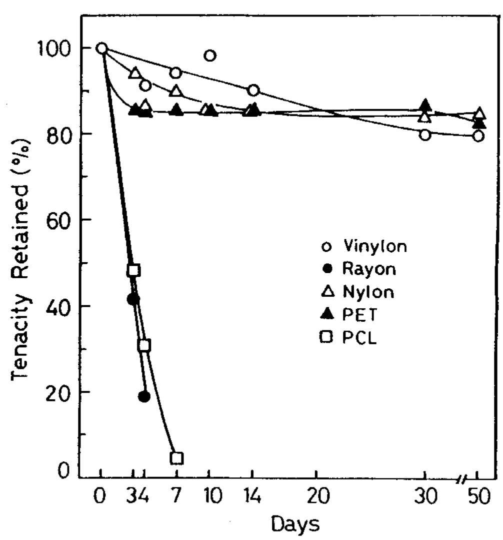


FIG. 2. Soil burial tests of various kinds of fibers.

CONCLUDING REMARKS

Cellulose is an excellent material gift from Nature to human beings. From the viewpoint of chemical structure, cellulose has rigid segments consisting of pyranose rings in the chain, and has a large number of intermolecular hydrogen bonds. It has high crystallinity. It does not melt. It shows a good fiber-forming nature. Its fiber exhibits a high Young's modulus. Moreover, by introducing various functional groups or modifying intramolecular hydrogen bonds, there is the possibility of a variety of cellulose derivatives for fibers, fabrics, and other products.

The invention of Tencel proved that developing technology can draw on the superior potential of cellulose, and it strongly suggests there may be further development of cellulose in the future.

Recent developments of cellulose-related products such as membrane and nonwoven fabrics are significant. It has been shown that progress in functional after-treatments for cellulose fibers and fabrics can be applied to both cotton and regenerated cellulose. This development is closely related to the development of cellulose chemistry research [5]. The high activity in basic research on liquid crystalline cellulose has brought hope for the development of new functional materials.

Cellulose represented by rayon is very promising as a fiber material in the future. Among many superior properties, high moisture regain and good affinity for the human body are especially suitable for clothing in warm and humid regions like East Asia and Japan. The good biodegradability of rayon described in the previous section is useful from the viewpoint of environmental protection. In the long-term forecast, complete recycling will be desired of synthetic fibers for clothing and other usages, and then the economic advantages will be reduced. Also, it must face the limitation of material resources, even though that will not be as severe as for foods. The supply of cellulose from Nature is stable and enormous (much more if chitin is included). Cellulose is very much a polymer from natural sources. Therefore, it is highly desirable that the skills of humans should be concentrated on cellulose chemistry and the related industry represented by rayon.

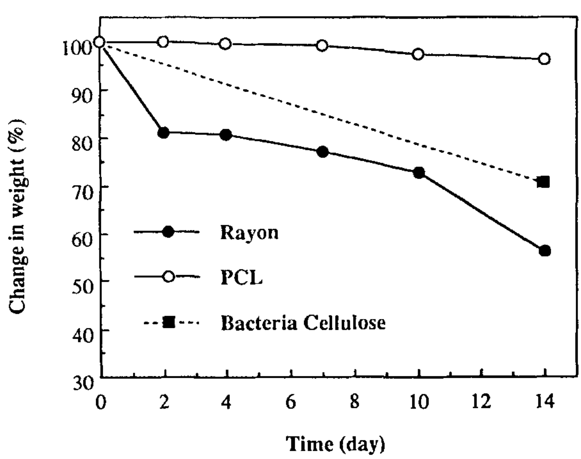


FIG. 3. Soil burial tests of rayon film and others fibers.

APPENDIX

Statistics on fiber production are presented as Figs. A-1 (rayon yarn), A-2 (rayon staple), and A-3 (various fibers), and A-4 (rayon and acetate).

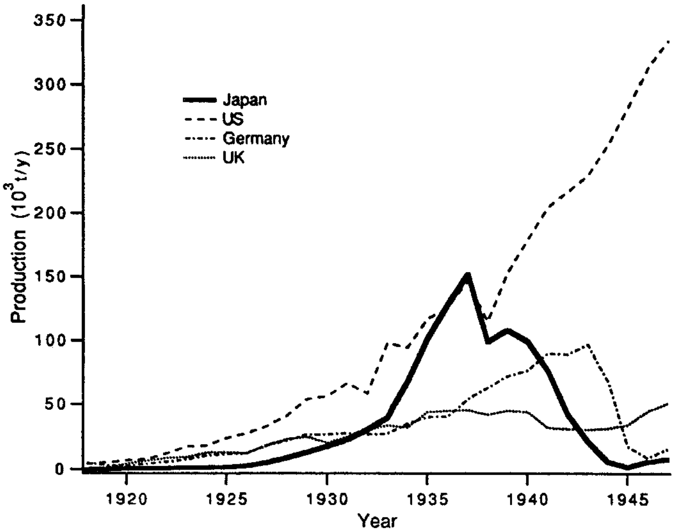


FIG. A-1. Production of rayon yarn in several countries.

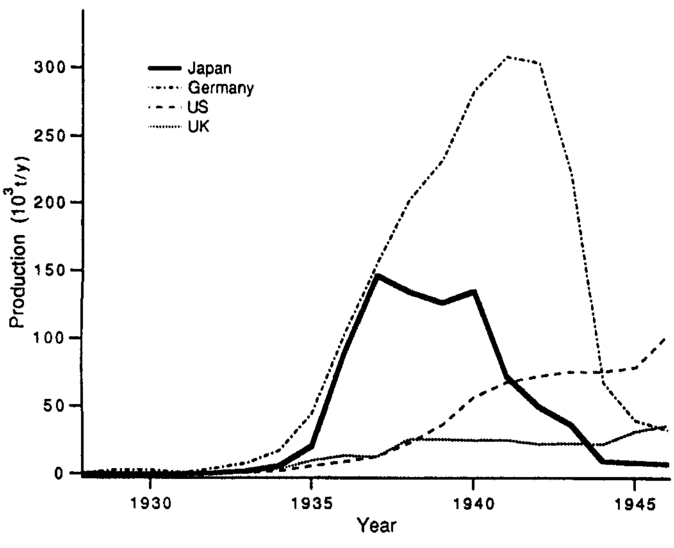


FIG. A-2. Production of rayon staple in several countries.

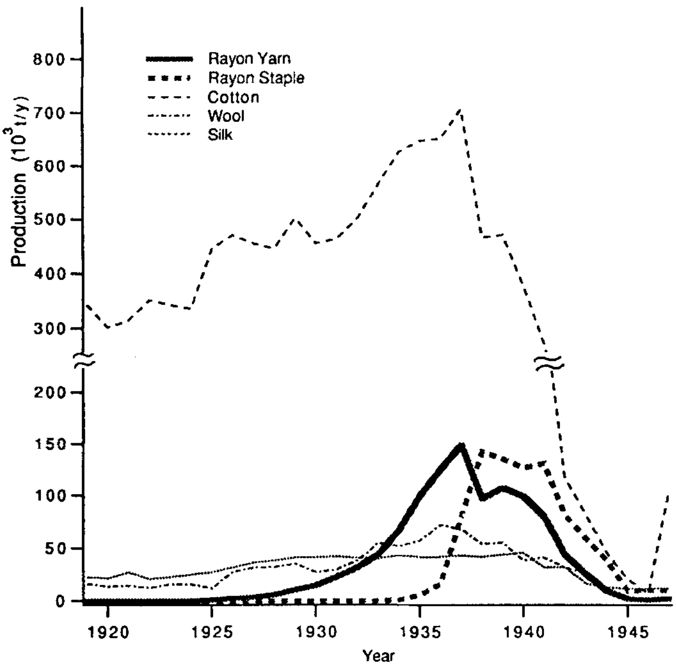


FIG. A-3. Production of fibers in Japan.

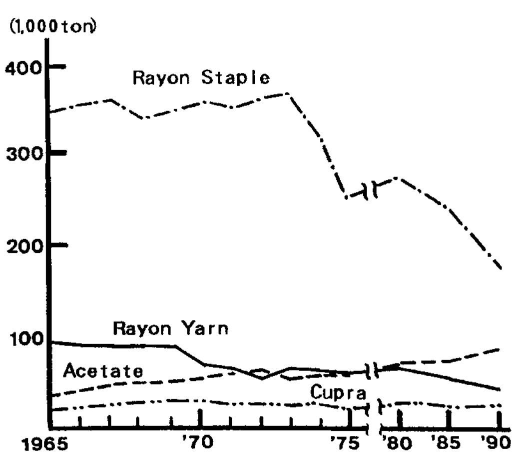


FIG. A-4. Production of rayon and acetate in Japan.

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