

Nylon plastics technology

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Preface

The nylons emerged as commercial engineering thermoplastics after the Second World War following their remarkable wartime success in the textile field. The large-scale production of nylon plastics grew mainly from the adaption of conversion methods and equipment already used for other thermoplastics, together with the availability of relatively cheap raw materials for bulk manufacture of the polymers. The premium properties of the nylons quickly led to their acceptance and use as high-grade engineering plastic materials.

In this volume an attempt has been made to present, for the use of students taking technology courses in colleges and for technologists in the nylon industry, a broad but balanced picture of present-day nylon plastics technology. The chapters follow the sequence adopted for other monographs on plastic materials in this series, and cover raw materials, chemistry, properties, conversion processes and applications, with an historical introduction and a final chapter on analysis and testing.

While the emphasis is largely on the technology of the nylons, there is coverage of the scientific aspects and theory sufficient for the needs of most technologists. In discussing properties the need is emphasised to obtain and use reliable design data to exploit fully the unique combination of properties possessed by nylons.

In compiling this book a large number of references were consulted, and those from which data were selected for inclusion are listed at the end of each chapter. Particular acknowledgement must be made to Carl Hanser Verlag, publishers of *Kunststoff-Handbuch*, for permission to reproduce a number of diagrams and tables from Vol. VI (*Polyamide*); also to Imperial Chemical Industries Ltd, Plastics Division, E. I. Du Pont de Nemours and Co. (Inc), Plastics Department, the Polymer Corporation, and Polypenco Ltd, for permission to make extensive use of information and diagrams appearing in their technical service notes, brochures and manuals.

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Introduction

1.1 General

The ever-increasing use of plastics in civilised society is now recognised as a significant contributory factor to an increased standard of living. Indeed it could be said that a country's prosperity can be measured by its plastics production in much the same way as sulphuric acid production was quoted as the index in the early years of this century.

The establishment of large-scale plants for manufacture of plastics materials (particularly in the United States but also in Europe, Japan and elsewhere) made available for world markets in the 1960s an abundance of cheap but high-quality material that could be converted to the shapes, forms and finished products familiar to all of us today. Generally the technology that led to this growth is now well known, and international and national companies are producing more or less standard plastic materials using techniques either developed by themselves or obtained by licence agreements from others.

The economic status of polyamides in relation to other plastics can be assessed from published statistics of sales, production and usage; these are presented in detail in section 1.3, and it is clear from them that polyamides account for only a small percentage of total plastics production.

The unique position of polyamides in the plastics field is, however, due largely to their high strength and toughness, which properties bring them into the sphere of conventional engineering materials. Allied to this is their high melting point yet thermoplastic behaviour, which allows of their processing by conventional extrusion and moulding.

The aim of this monograph is to review the science and technology of polyamides with special emphasis on their properties and applications. An account of the raw materials used in the manufacture of polyamides is included to show their relationship to organic chemicals generally.

1.2 Historical

The decision of E. I. Du Pont de Nemours & Co. (Inc.) to embark on fundamental chemical research in 1928 marked the beginning of a new age of chemical discovery for the company¹. To initiate this work Du Pont appointed Dr Wallace N. Carothers of the University of Illinois. Carothers, who at 32 had a high reputation as an organic chemist, was allowed to select his own line of research and was given ample funds to carry it out. Carothers was fascinated by the natural polymers in the animal and vegetable kingdoms—for example, wool and silk. His proposal was to try to synthesise them. Using dibasic organic acid and di-hydroxy alcohol, Carothers was able to synthesise large molecules showing colloidal behaviour, but real success came in April 1930: his colleague Dr J. W. Hill, by using the technique of the molecular still to remove effectively the water produced by condensation, was able to produce a tough elastic material which, although it could be drawn into a fibre, was still brittle. Carothers named these materials 'super-polymers', but because of their low melting point and their solubility in common organic solvents he deemed them unworthy of further detailed investigation. So, switching his attention to polyester amides and polyamides, he found that these materials conformed more to his ideal 'super-polymers'. In May 1934 he demonstrated the production from polyamides of fibres that were heat resistant and stood up to washing and dry cleaning. Many more polyamide 'super-polymers' followed and by 1935 polyamide 66, better known as nylon 66, was judged to be the material with most promise. The pure research on the super polymers was succeeded by applied research on polyamides, particularly nylon 66. A pilot-plant was built to produce monofilaments and film. On 27 October 1938 Du Pont announced their development of a new 'group of synthetic super-polymers' from which could be produced high-strength textiles. The super polymers were said to be protein-like in character and the generic name 'nylon' was applied to them.

The properties of the new material caught the imagination of the American public when it was demonstrated that the fibre had superior mechanical properties to natural silk. Ladies' stockings made from the new material were exhibited at the New York World Fair in 1939 and in a Chicago Fair in the same year. In May 1940 nylon stockings were on sale in stores in the US. Demand soon exceeded supply, and plants to produce the nylon polymer and yarn were erected in many parts of the US. At this time the market was

mainly for hose, toothbrush bristles and sports gear, but many other textile applications were found.

The outbreak of hostilities with Japan in 1941 cut off the importation into the US of Japanese silk, but fortunately nylon was there to take its place.

Carothers died in April 1937 at the age of 41, so did not live to see the full realisation of his polymer research work. During his nine years with Du Pont more than fifty patents were issued in his name and about as many scientific papers².

While Carothers was working in the States, laboratory work on polycondensation of esters and amides was being carried out by I. G. Farben in Germany. As with Carothers no useful fibre-forming materials were found in the early work, and during the economic depression of the 1930s work was suspended. The disclosures by Du Pont, in patents and other publications, of success in the field of fibre-forming materials led to resumption of the German work. Success came when Schlect in 1938 showed that by careful selection of catalysts—including aminocarboxylic acids, 66 salt and water—the caprolactam ring could be opened and straight-chain polymerisation effected. The stability and ease of purification of caprolactam brought success in the early experiments and high polymers were produced with properties very similar to nylon 66. The high polymers from caprolactam were designated 'Perlon'.

In 1939 a licence agreement was arranged between I. G. Farben and Du Pont, who meantime had published a large number of patents on the spinning and drawing of polyamides³. With the possession of much of Du Pont's know-how in fibres the pace of development quickened, and in 1939 the first production form of 6-polyamide (termed 'Perluranborsten') was produced in I. G. Farben's Berlin-Lichtenberg factory and became commercially available. Technical work continued during the Second World War, and injection-moulded parts in nylon 6 and 66 were produced and tested in service. The work at I.G.'s Ludwigshaven plant was on developing the use of nylon as a plastic material rather than as a fibre, which had hitherto been Du Pont's main nylon product.

After the war Du Pont quickly adapted their market to the plastic as opposed to the fibre uses of nylon. Other countries—the UK, France and Holland—quickly followed the two leading nations in polyamides and set up plants for both fibre and plastics production of polyamides.

The above historical outline of the discovery and development of polyamides would be incomplete without mention of Carothers'

basic ideas on molecular chain growth in polymerisation⁴. He believed that the synthesis of linear giant molecules could only be achieved by head-to-tail condensation reactions involving small molecules each of which had bifunctionality, i.e. one reactive group at each end of the molecule. Carothers defined functionality in a monomer as an arrangement of atoms that could lead to a reaction step, e.g. $-\text{OH}$, $-\text{NH}_2$, $-\text{COOH}$ and so on. According to the number of such units in the monomer (one, two or more) the monomer is called monofunctional, bifunctional, etc. Carothers discovered that, if such bifunctional monomers were used that on reaction could form five- or six-membered rings by intramolecular reaction, this was the preferred mode of action. However, if rings larger than six were possible by intramolecular reaction, linear reaction occurred preferentially. The Sachse-Mohr theory may be invoked in support of the observation of the preferential formation of five- or six-membered rings from bifunctional monomers.

The use of the molecular still was undoubtedly the basis of Carothers' success in producing useful high-molecular-weight polymers. Previously molecular weights of only about 5000 had been achievable. Using the still the molecular weight could be raised to over 10 000 because the low rate of diffusion of volatile products of condensation and the tendency for them to remain dissolved or absorbed could be overcome.

Carothers had to choose for detailed study either the tougher, less easily fusible and less soluble of the polyamides he obtained from ϵ -aminocaproic acid or the strong, pliable, highly-oriented (but low-melting-point and soluble) polyester-polyamides. His concentration on the mixed super-polymers may have been the reason for his failing to develop polycaprolactam as a useful fibre, thus allowing the Germans time to develop the catalytic system which was used to polymerise ϵ -aminocaproic acid so successfully in the work which eventually produced 'Perlon'.

1.3 Present status of the industry

The growth of the plastics industry, which includes polyamides, is conveniently observed in published statistics. Those believed to be accurate and reliable are published annually in *Europlastics* and *Modern Plastics*; figures are available on sales, production and consumption of all plastics, allowing year-by-year comparison to show growth rate. The data refer only to the US and the UK, the

former being by far the world's largest producer of nylon plastics. The trends in growth-rate and end-use of nylons throughout the world can be expected to follow closely the American and British pattern.

Table 1.1 shows the total sales of nylon in the US in the period 1962–1973. (In this and other tables in this section all quoted figures have been converted to units of 1000 tonnes to aid comparison.) Thus for the US alone, the major producing country, sales more than quadrupled during that time.

Table 1.1 SALES OF NYLON (ALL TYPES) IN US, 1962–1973 (data from *Modern Plastics*, annual January issues)

Year	1962	1963	1964	1965	1966	1967	1968	1969	1970	1971	1972	1973
Total sales (1000 t)	18.6	20.1	22.3	27.2	27.6	27.7	34.5	40.2	46.0	49.9		
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Table 1.2 SALES OF PLASTICS IN US IN 1972 AND 1973 ALLOCATED TO TYPE (data from *Emroplastics* (British Plastics Edition), Jan. 1973, 1974; *Modern Plastics*, Jan. 1973, 1974)

Thermoplastics type	Sales (1000 tonnes)	
	1972	1973
Polyolefines	4200	4896
PVC (Polymers)	1975	2171
Polystyrene	2111	2407
Polyvinylacetate	370	391
Cellulosics	75	77
Acrylics	208	233
<i>Thermosetting type</i>		
Amines	411	464
Alkyds	290	342
Phenolics	651	654
Epoxides	83	99
Polyesters	416	496
Polyurethanes	493	593
Miscellaneous*	110	122
Total	11393	12945

* Includes acetal, fluoroplastics, nylon, polycarbonates, silicones, etc.

There are no reliable statistics that show the proportion of nylon sales to total plastics sales. Some indication is, however, given in *Table 1.2* of sales in the US for 1972 and 1973 for all plastics. The miscellaneous group, which includes nylon, comprises only 9.7 per cent of total sales in 1972 and 9.5 per cent in 1973. It is evident that on sales tonnage in the US nylon ranks very low among plastics materials. Expressing sales on a cost basis would considerably improve the ranking of nylon since it is a relatively high cost material. However, polyamides as a class are and will remain for a long time low-volume, high-cost plastics.

The allocation of nylons to particular end-uses, shown for UK and US consumption in *Table 1.3*, indicates one reason for the comparatively low tonnage of nylon sales and production compared with other plastics. The table shows the major uses to be for automobiles

Table 1.3 NYLON CONSUMPTION IN UK AND US IN 1972, 1973: ALLOCATION TO END-USE (data from *Europlastics* (British Plastics Edition), Jan. 1973, 1974; *Modern Plastics*, Jan. 1973, 1974)

	Consumption (1000 tonnes)			
	UK		US	
	1972	1973*	1972	1973
<i>End-use</i>				
Appliances			5.3	6.1
Automobiles and trucks			13.9	16.0
Building and construction	0.2			
Land transport	1.4			
Consumer products	1.5		3.9	5.0
Electrical and electronics (including communications)	0.4		9.0	11.5
Fancy goods	0.1			
General industry	3.1			
Machinery parts			6.6	9.2
Housewares	2.1			
Others (including exports)			8.0	10.6
<i>Extrusions</i>				
Filaments			6.9	7.2
Film			5.7	5.0
Sheet, rod and tube			3.4	4.0
Wire and cable			3.8	4.2
Totals	8.8		66.5	78.8

* Statistics not available

and trucks, electrical and general industrial outlets. These are, of course, generally engineering applications. The adoption of plastics as metal replacements in established all-metal designs has been slow mainly because of lack of engineering data and practical experience. Confidence is rapidly growing in this field as design data becomes more readily available, and the use of polyamides in automobiles is rapidly increasing. The development of reinforced grades of nylon and new fabrication techniques will undoubtedly accelerate progress.

The use of nylons in housewares must not be overlooked, and in applications where its lightness, toughness, strength and temperature resistance can be used with advantage it will be accepted.

The figures given in *Table 1.4* show the all-nylon consumption in the UK and US during the years 1972 and 1973. The per capita consumption based on the population of the two countries (UK population in 1971 census 55 million, US population estimated in 1970 at 203 million) shows an almost equal usage in the two countries.

Table 1.4 NYLON CONSUMPTION IN UK AND US IN 1972, 1973 (data from *Europlastics* (British Plastics Edition), Jan. 1973, 1974; *Modern Plastics*, Jan. 1973, 1974)

	1972		1973	
	UK	US	UK	US
Total consumption (1000 t) of all nylon	18	66.5	21	78.9
Consumption (1000 t) per 10 ⁶ capita of population in each country	0.33	0.33	0.38	0.39

The observations from the statistics tabulated are the author's own and without more detailed knowledge of their derivation it would be invalid to make more than the broadest generalisations.

1.4 Future developments

Because of the rapid pace of innovation in plastics it would be unwise to predict developments in polyamides beyond the mid-1980s. For the decade to 1985 likely developments in raw materials, processes, and fabrication or conversion techniques are briefly discussed in the following paragraphs.

1.4.1 MATERIAL DEVELOPMENT

There is unlikely to be a major improvement in the present range of properties of polyamides through the synthesis of new members of the class, because all the obviously feasible arrangements around the carbo-imide group characteristic of the class seem to have been examined already.

A great deal of effort, however, will be put into improving the present properties, and a much wider range of nylon polymers, each tailored to a specific application, should become available. These will include heat-resistant types containing aromatic groupings along the chain, fire-resistant types, and types of higher deflection temperature—produced for example by controlled cross-linking using appropriate catalysts, or by external means such as high energy radiation.

The present trend of modifying polyamides by the use of fillers will continue, but advances in this area will depend upon success in solving the problems associated with filler-matrix compatibility, and filler adhesion and dispersion. In the engineering field the design parameters of any new material must be established as early as possible, preferably before marketing, so that designers and engineers can adopt the material with a reasonable degree of confidence.

Environmentally resistant types of polyamides will be generally available when the present generation of UV heat and hydrolysis-stabilised types that have been patented in the last few years have been critically examined under service conditions, and those that have stood the test of time have been selected for further development.

1.4.2 RAW MATERIAL PROCESS DEVELOPMENT

Novel processes for producing the present or new polyamide types will continue under active investigation. The preoccupation with size for the fabrication of large engineering parts puts a strain on the traditional methods of fabrication through injection moulding and extrusion, and the direct conversion method exemplified in the process of anionic polymerisation of caprolactam is regarded with great favour. Similar systems stand a good chance of being commercially successful as the result of stimulating competition from other similarly derived polymers, such as the solid polyurethanes.

1.4.3 CONVERSION AND FABRICATION DEVELOPMENT

With the hardening in design in injection moulding and extrusion, machinery development in this area will be concerned with increased size and sophistication. Major advances are unlikely. The ICI sandwich moulding process⁵, which injects two polymer formulations into the mould sequentially to form a composite structure of a core and skin each with its own properties, is likely to be fully developed for polyamides. The Engel process⁶, which uses ultra-high pressure and catalysts to cross-link linear polymer chains, might well be applied to polyamides if suitable chemical techniques are found.

Rotational moulding will be more widely used, particularly for larger fabrications.

The techniques of solid-phase forming of stock shapes and fabricated parts, which are slowly improving as the basic problems are being solved, should permit further useful alternatives in the fabrication methods available for polyamides.

For small precision parts requiring good dimensional stability, the technique of powder sintering (developed originally for metallic components) will be used more generally for polyamides in the replacement of metals by plastics for automotive parts and for small mechanical components.

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Raw materials for polyamides

2.1 Introduction and terminology

The term nylon is applied to the synthetic polyamides that have fibre, film, and/or plastic-forming properties. All nylons have in the polymer materials the amide ($-\text{CO}-\text{NH}-$) group, the link that joins the repeating hydrocarbon units of various lengths. The intermediates for nylons are dicarboxylic acids, diamines, amino acids and lactams. The nylons are usually identified numerically using the number of carbon atoms in the basic units of the polymer chains. A duplex digit is used where the nylon is derived from a diamine and diacid, the first digit of the duplex referring to the diamine. For example, the polymer from adipic acid and hexamethylene diamine is termed nylon 66, that from sebacic acid and hexamethylene diamine nylon 6.10, that from caprolactam nylon 6. The terms nylon and polyamide are used interchangeably in commercial and technological publications.

2.2 Economics

The world volume of production of polyamides was until recently closely affected by the price and availability of feedstock for the intermediates; in the latter half of the 1960s, however, production became much more dependent on the ability to sell the product in the form of fibres in competition with the acrylic and polyester fibres, which were gaining a much larger share of the fibres market. At the same time the processes of conversion of raw materials to intermediates (which started with the original commercial processes used by Du Pont and I. G. Farben) continue to be a fertile field of innovation aimed at reducing costs and offering alternative routes to the product.

For new intermediate plants starting up, the choice of route depends both on feedstock price and availability and on the market for by-products—particularly, in the case of polyamides, ammonium

sulphate, which for most processes is the by-product produced in greatest amount. Ammonium sulphate is used in the fertiliser industry and the demand for it is subject to long-term variation.

The main commercially-used routes to the nylon intermediates, with their advantages and disadvantages, are described in the following sections.

2.3 Feedstocks and intermediates

Feedstocks for the commercial polyamide intermediates are with few exceptions aromatics, cyclohydrocarbons, or olefines derived largely from the petrochemical industry. One exception is castor oil, which is the precursor of both sebacic acid (a component of nylon 6.10) and also undecanoic acid (the intermediate for nylon 11).

2.3.1 INTERMEDIATES FOR NYLON 66

2.3.1.1 Adipic acid

The usual process for adipic acid intended specifically for nylon 66 uses the nitric acid oxidation of cyclohexanol or KA oil (mixture of cyclohexanol and cyclohexanone). The latter is reacted with dilute nitric acid (about 60 per cent) at 60–110°C in the presence of a mixed ammonium vanadate catalyst. The yield is claimed to be over 90 per cent and the conversion rate is high.

The advantage of this process is its simplicity and its ability to produce material of high purity at high conversion rate. The disadvantage is the large nitric acid consumption and requirements for nitric acid recovery.

This process can be combined with the process for making KA oil from cyclohexane discussed in greater detail in section 2.3.2.1(a)(ii).

Adipic acid produced by this process can be made the starting material for hexamethylene diamine, the other monomer for nylon 66, although many other processes exist (see section 2.3.1.2).

Considerable development work on other adipic acid processes is described in the technical literature¹.

2.3.1.2 Hexamethylene diamine (HMD)

The adipic acid process and the butadiene process described below account for most of the world production of HMD. These and other processes used industrially are shown with flow diagrams in *Figure 2.1*. The considerable number of processes available for HMD

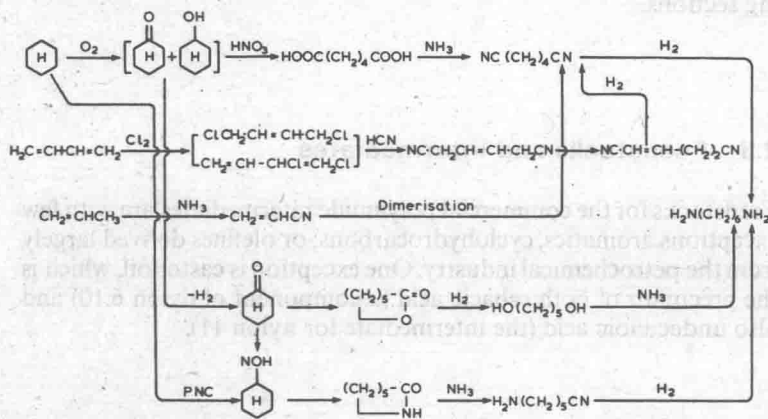


Figure 2.1 Commercial hexamethylene diamine processes (courtesy *Chemical Economy and Engineering Review*)

production indicates the key role of this intermediate in effecting economies in nylon production.

(a) Adipic acid process

This process has the advantage that the HMD can be produced in a series of steps starting with adipic acid, the other monomer for AH salt (nylon 66 salt). The first step consists of vaporising the adipic acid in ammonia gas and dehydrating the mixed gas in a reactor over a suitable catalyst to obtain the nitrile. Some of the acid is lost by decomposition at this stage and yield is reduced. (Considerable development work protected by patents and aimed at improving the efficiency of this part of the process is being undertaken by several large raw-material producers.) The second step, hydrogenation of adiponitrile, is usually carried out in the liquid phase at high pressure over a nickel or cobalt catalyst. Here again several variations in the

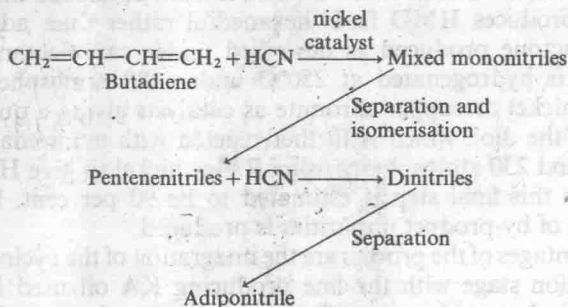
method, involving reactor type, reaction conditions and catalyst, are known.

The adipic-acid route to HMD has no major disadvantages, and the process is used by the majority of the large raw-material suppliers.

(b) Butadiene processes

The original process was developed and is used commercially by Du Pont. The flow diagram is shown in *Figure 2.1*. Adiponitrile is obtained almost quantitatively and its hydrogenation follows the same steps as in the adipic-acid process. While the butadiene process has the advantage of low cost of butadiene feedstock and good conversions and yield, considerable quantities of hydrocyanic gas and chlorine are used and capital costs are high. To obviate the use of chlorine in this process, Du Pont have recently developed and commercialised a new route from butadiene^{2,9} which, it is claimed, results in a saving of 15 per cent over their older process for making adiponitrile.

The reaction steps in the improved process are shown below in diagrammatic form:



Another route to adiponitrile using butadiene as starting material has been developed by Esso Research and Engineering². This process involves reaction of butadiene with iodine and cuprous cyanide to give the cuprous iodide complex of dehydroadiponitrile, which is further reacted with HCN to give a high yield of dehydroadiponitrile and regeneration of the iodine and cuprous cyanide. The recycling of the complexing components makes this process economically attractive.