Aromatic Polyamide Fibres

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THE aromatic polyamide fibres are widely used today. The properties like good heat resistance, tensile strength and impact strength make them suitable for application in fields like aerospace and marine industry. The development of high temperature and flame resistant fibres has gone mainly along two lines:

  (i) by modifying the ordinary fibres by post-treatment to make them flame resistant, and

  (ii) by preparing special type of fibres which are inherently resistant to high temperature and flame. The aromatic polyamide fibres belong to the second category. They possess superior mechanical properties and therefore, can replace metal alloys in aerospace industry.

A wide range of polymer compositions has been developed with high strength and flame resistant properties and most of these materials fall within the class of polymers known as "aramids".

This review deals mainly with those polymers which are inherently flame resistant and have a high content of aromatic groups.

Synthesis

The aromatic polyamides are produced by melt polycondensation, solution polycondensation or interfacial polycondensation. In general, reactants (diamines and diacids/chlorides) are blended in equimolar proportions to achieve high molecular weight products. When one of the reactants is used in excess, the lower molecular weight species are also obtained.

Melt polycondensation — Aliphatic polyamides, one of the most important classes of condensation polymers, have been prepared by this process. In the case of aromatic components, this method has several drawbacks, such as (i) low reactivity of diamine and (ii) decomposition of the reaction mixture. Many
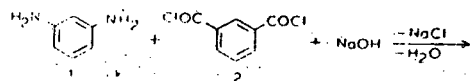
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Fig. 1 — Route for aromatic polyamide production

of these polymers have high melting points and therefore, they cannot be melted without decomposition; hence, this method is generally not suitable for preparing this class of polymers.

Interfacial polymerization[1-25] — The aromatic diamines are, generally, inactive and hence, in interfacial polymerization the condensation is effected by using more reactive diacid chlorides. This method involves dissolving of the diamine (1) in water with an acid acceptor (Na_2CO_3 or NaOH) and the diacid chloride (2) in an immiscible solvent. The extent to which the reaction proceeds depends on various factors. Some of these are as follows:

Reaction conditions — For high yield the temperature is kept at 5-10°C[11] with high speed stirring.

Purity of reactants — The reactants are carefully purified; the diamine is purified by fractional distillation and vacuum sublimation and the acid chloride is distilled under high vacuum. The optimum mole ratio of diamine to acid chloride has been found to be in the range 0.9-0.93.

Type of solvent-water interface — The preparation of aromatic polyamide was reported by Russian workers. Beaman et al.[13] prepared poly(*m*-phenylene-phthalamide) using benzene-acetone-water system with inherent viscosity 0.73 (74% yield). Later, Morgan et al.[14] prepared polyamides using dichloromethane-water mixture. Katz[15] reported the preparation of polyorthophthalamide of bis(4-amino-3-methylphenyl) methane in chloroform-water with an inherent viscosity 0.35 (89% yield). The low inherent viscosity in this case is most probably due to chain termination through imide formation and not due to low polymer-solvent interaction or the low reaction rate. Sokolov et al.[16-18] prepared a number of wholly aromatic polyamides under different conditions. It was found that products of comparatively high molecular weights were obtained in dilute solutions in poor solvents and in aqueous acidic phases. Fedotova et al.[19-21] attempted the preparation of aromatic polyamides using benzene and CCl_4 as solvents with dilute solutions in 0.005-0.05 M range. The reduced specific viscosities were <0.5 for 16 out of 20 polymerizations; these are comparable to those obtained in high temperature reactions between diamines and acid chlorides. Poly(sebacyl benzidine) was produced with the highest solution viscosity in an acid medium, whereas the other polymers required 2-2.5 moles of KOH/mole of diamine.

The only consistently successful two-phase method for preparing wholly aromatic polyamides is that of Hill et al.[22], in which the polycondensation procedure was modified by using inert polar organic liquids, such as cyclohexanone, tetramethylene sulphones and tetrahydrofuran. Polyamides were produced in nearly quantitative yields with inherent viscosity 0.6-2.5. If these polar solvents are water-miscible or at least partially water miscible, the less basic acid acceptors are preferred for minimizing the acid chloride hydrolysis. Even bicarbonates can be used for hydrolysis because the aromatic diamines are very weak bases. The use of solvents with appreciable water miscibility appears to be contrary to the original definition of the interfacial polycondensation method and to all preceding comments on the detrimental effects of phase miscibility. The improvement realized by the use of water-miscible solvents does not arise from the potential miscibility of the phases. The advantage comes from the use of polar solvents which are better solvents or swelling agents for many condensation polymers than are the hydrocarbons or chlorinated hydrocarbons used previously. In these solvents, the reaction rate is enhanced because of the increased polarity of the medium[23-25]. The polymerization is believed to take place near the interface of a two-phase liquid system.

Solution polymerization[26-56] — In this method, the fast reacting intermediates are brought together in an inert liquid medium and the acidic byproducts if any, are removed by means of basic additives (acid-acceptors). The diamine is taken in a suitable solvent and mixed rapidly with the acid chloride in the same solvent. Tertiaryamine is employed as an acid acceptor. Kwolek et al.[26] suggested another variation in the solution polycondensation method, applicable to aromatic diamines and other weakly basic intermediates, in which a weakly basic organic liquid serves both as solvent medium for polymerization and as an acid acceptor. Examples of these media are tetramethylurea[29], tetrahydrofuran[31], dimethylacetamide[29,30,31,35], N-methylpyrrolidone[28,30,32-35] and hexamethylphosphoramide[32,34,35]. These amides are all much weaker bases[27] than primary aromatic diamines, but by using an excess of an amide, the polymerization is brought to completion without any loss of diamine as an inactive hydrochloride. An important feature of this type of polycondensation is high yield with moderately fast reaction. However, the important prerequisites are: (i) adequate amounts of the solvent and the acid acceptor, (ii) purity of the solvent and the reactants, (iii) proper degree of mixing and stirring, (iv) proper selection and control of solvent, and (v) duration of reaction.

Mechanism of Formation

A successful polymerization in the presence of amine acceptor is shown in Fig. 2.
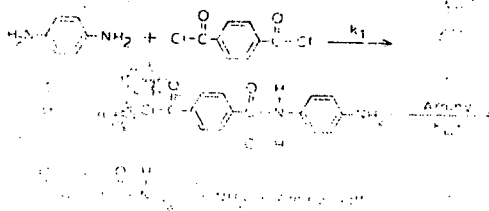

Fig. 2 — General mechanism for polyamide formation $[k_{II+} > k_I > k_{reactant\ mixing}]$

solvents could be prepared. This has not been possible in the case of polyamides containing only phenylene units. In the case of heterocyclic amide copolymers, the heterocyclic in effect replaces two amide linkages and a phenylene unit of the ordered copolyamides as shown in Fig. 5. The effect of the 6-membered heterocyclics in aromatic polyamides has been little studied.
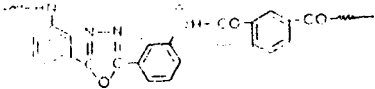

Fig. 5 — Mode of replacement of amide links by heterocyclic unit

(4) In case of polyamides derived from *p*-isomers of acid chloride and diamine, the *para* phenylene content decides the solubility as well as rigidity and modulus. But processability is improved by the incorporation of the *meta* components. Certain copolymer compositions with requisite solvents have been developed[32-56].

Preparation of Fibres

Aromatic fibres have been obtained both by wet[57] and dry[58] spinning procedures. Good quality fibres are obtained from anisotropic solutions as observed by the appearance of a maximum in the solution viscosity-polymer concentration relation[59]. Up to the maximum solution viscosity, the system behaves as a normal isotropic one. But further increase in polymer concentration lowers the solution viscosity. This is due to the transformation from isotropic to partially anisotropic liquid crystal state, where the polymer molecule exists in the fully extended form; this helps in obtaining fibres in partially oriented state. The parameters defining the production of an anisotropic dope are solvent type, polymer molecular weight and solution temperature[60].

Solvents used for the Preparation of Spinning Dope

Highly polar solvents like dimethylacetamide (DMAC), hexamethylphosphoramide, N-methyl pyrrolidone and dimethyl formamide with LiCl or CaCl₂ are used. In the case of poly (*m*-phenyleneisophthalamide), direct spinning is possible by carrying out polymerization in suitable solvents[16-33]. These are wet spun at room temperature into water[23,49,50] or dilute H₂SO₄ coagulants. The fibres are then washed thoroughly and dried. The major breakthrough came with the application of the dry jet wet spinning process where the spinneret is kept at about 1 cm above the coagulation bath. The advantages of dry jet wet spinning are: (1) the spinning dope can be kept at high temperatures and hence, higher polymer concentrations can be obtained; (2) the shear stretch applied to the dope during extension increases orientation and hence eliminates the expensive post-heat treatment. The tensile strength of the as-spun fibres depends on the type of the solvent and decreases in the order[61]: DMAC > DMSO > DMF. Depending on the sol-

vent used, any of the following coagulating baths is employed.

(1) Triethylamine and acid acceptor (Na₂CO₃ or NaOH) below 20°C[62]
(2) 35·4 parts triethylamine and 1000 parts tetrahydrofuran (THF) at 5°C[62]
(3) 3 parts H₂O and 7 parts MeOH[63]
(4) 8% aq LiCl at 19°C and at 28°C
(5) 5% aq LiCl at 19°C[64]
(6) Tetramethylurea and 6·5% LiCl at 140°C[35]
(7) 43 wt% CaCl₂ at 60°C[28]
(8) Aq KCl[2]
(9) Dipropylene glycol bath at 65°C[12]
(10) 91 parts hempa (solvents optionally contains metal halide) and 5% LiCl[12].

Reports are available on the use of surfactants in coagulation baths where they help in drawing of fibres at 85° in water[65] and bring along partial orientation of the fibres. The rate of spinning also has an effect on orientation and hence on the mechanical properties.

Properties and Uses

Numerous reports are available on the preparation of a variety of polyamides which have been evaluated in fibre form under experimental or developmental programmes[54-56]. Commercial exploitation has been possible with two types of fibres: 'Nomex', poly(*m*-phenyleneisophthalamide) and 'Kevlar', poly(*p*-phenyleneterephthalamide). Both these fibres have an excellent balance of physical and chemical properties and have wide utility in industrial and military applications. The production of Kevlar has been growing steadily. There are three different types of Kevlar, viz. Kevlar, Kevlar 29 and Kevlar 49; the last one is of high modulus type obtained with maximum heat treatment and orientation. On weight basis, the tensile strength of Kevlar is almost twice that of glass and five times that of a steel wire. Its tensile modulus is 50% greater than that of steel wire.

Aromatic polyamide fibres have been characterized by X-ray studies. Nomex is shown to have a triclinic cell with *a*, 5·27; *b*, 5·25; and *c*, 11·3Å (fibrosis), α, 111·5; β, 111·4; and γ, 80° with crystal density 1.47 g/ml. The amide group and aromatic ring are not coplanar, because the ring hydrogen interferes with hydrogen bond formation. This steric hindrance is overcome by hydrogen bonding of the amide group, perpendicular to the aromatic ring. In the case of *meta* oriented polyamides, the molecules in the crystal are contracted by 1° per monomeric unit from the fully extended conformation and hence possess lower tensile strength and greater elongation compared to the *para* isomers (Table 1). From the moisture regain data, the crystallinity of Nomex is found to be 47%.

The melting points of aromatic polyamides are directly related to the orientation (*ortho*, *meta* or *para*). On comparing the fully *para* oriented polymer, it is observed that the melting point is higher by 100°C in the latter, whereas *ortho* substitution lowers the melting point. Similarly, incorporation of naphthalene or biphenylene rings increases the melting point. In all these cases, the glass transition temperature is above 250°C. This has a practical significance

For giving a suitable explanation for the polycondensation system, it is necessary that the amide-forming reactions meet the following requirements:

(1) The acylation rate and proton affinity of the amine groups are presumed to be proportional to their base strengths.

(2) Amine hydrochlorides or protonated amines are not acylated by acid chlorides.

(3) The rate of reaction between acid chloride and amine is high, but the rate of removal of the portion or hydrogen chloride from the protonated amine in the presence of base is still higher. During polymerization, free diamine is the acid acceptor as long as it is available and it becomes weakly basic soluble monohydrochloride. Alternatively, an effective acid acceptor, such as tertiary amine is added, so that the polymerization proceeds to give high conversion.

Effect of Reactants

The polymerization is highly sensitive to the reactant concentrations and the volume ratio of the solutions. The preferred concentration range is 1-8 g reactants/100 ml solvent. Lower concentrations are uneconomical and introduce large amounts of solvent impurities. Higher concentrations may yield unstirrable masses and the heat of the reaction is difficult to control when the reactants are mixed rapidly.

Effect of Solvent

The solvent performs several functions: (i) dissolves the intermediates and helps in their mixing and contact, (ii) dissolves or swells the growing polymer, whereby the reaction is maintained, (iii) carries the acid acceptor and may affect the removal of byproduct salt, (iv) may affect the reaction rate by polarity, and (v) absorbs the heat of reaction. The selection of the organic solvent for interfacial polycondensation reactions is recognized as being related to the degree of polymerization[41,42].

Effect of Structure on Polymer Properties

Many modifications have been proposed in the skeleton structures of polyamides with the object of studying the relationship between the structure and the properties of the polymer and succeeded in the preparation of high molecular weight aromatic polyamides with excellent properties, such as high thermal stability and solubility. The properties of aromatic polyamides seem to depend primarily on the rigidity of the polymer chain/backbone. The fundamental skeleton structure of aromatic polymers is shown in Fig. 3. Considering the different types of groups substituted for Ar, it is possible to classify types of polymers as follows:

[—OCHN—Ar—NH.CO—]$_n$

(a) The diamine component can be diaminobenzene, diaminodiphenylmethane, diphenylene stilbene or even an ether or sulphide group or sulphoxide group containing diaminobenzene[7], and (b) the acid/acid chloride component can be varied over a wide range — aromatic, aliphatic or heterocyclic.

Several useful polyamides have been prepared based on the above possibilities and their properties have been evaluated in an attempt to establish a relationship between the structures and properties.

(1) When the skeleton is connected only with the benzene nucleus, para position gives polymers with higher decomposition temperatures and thermal stabilities than those obtained through meta- and ortho-substitutions. The melting points of aromatic polyamides are related directly to the orientation (i.e. ortho, meta or para) of the arylene units in the polymer repeating unit. For example, the replacement of all meta groups by para groups raises the melting point by 100°C. In general, incorporation of symmetrical naphthalene units and 4,4'-biphenylene unit in place of p-phenylene unit produces no significant change in the melting point of the polymer[43].

(2) The introduction of simple chains like —CH$_2$ groups between benzene rings in the diamine or substitution in the amide link increases the solubility. In the case of aliphatic-aromatic polyamides, N-methyl substitution results in marked lowering of the melting points. For example, when half of the amide linkages of the poly-isophthalamide of p-phenylene-N,N'-bisamino benzamide are replaced by N-methyl substituted groups, the melting point is lowered by 195°C. Such a decrease in the melting point in the wholly aromatic polyamides seems to be attributable as much to the disruption of orderly packing as to reduction of hydrogen bonding. Further, the lack of hydrogen bonding does not necessarily result in a low melting polyamide because of the fact that poly(2,5-dimethyl piperazine terephthalamine), in which there is no hydrogen bonding, has melting point 350°C. The introduction of heterocyclics like piperazine rings, o-, m- and p-phenylenedioxy linkages into the diamine produces polyamides with fairly high molecular weights. This substitution improves the solubility of the amide polymers in various solvents. The various groups lowers the melting point of polyamides as shown in Fig. 4.

(3) Since tractability is a problem in the field of thermostable wholly aromatic polyamide, both 5- and 6-membered aromatic heterocyclic unit, such as oxadiazole, thiazole, pyridine are incorporated. In fact, it was found that by the incorporation of certain 5-membered aromatic heterocyclics, polyamides having melting points above 500°C and soluble in organic
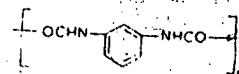

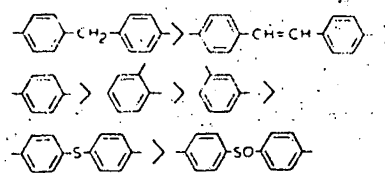Fig. 3 — Skeleton structure of aromatic polyamide

Fig. 4 — Various groups arranged in decreasing order of their ability to reduce the melting point of polyamide

TABLE 1 — PROPERTIES OF NOMEX AND KEVLAR

Fibre	Tenacity mN/tex	Modulus N/tex	Extension at break, %
Nomex	353	6·2	35
Kevlar	1850	41·9	4
Kevlar 29	1940	42·4	3·4
Kevlar 49	2540	89·5	2·8

TABLE 2 — PROPERTIES OF PPT FIBRE[54]

Heat treatment Temp., °C	Initial Modulus N/tex	Tenacity mN/tex	Extension %
As spun	15·3	618	9·1
500°C	78·4	~1207	1·6

in the sense that heat treatment of these fibers must be done at or above 250°C. It has been observed that the wholly aromatic fibres are amorphous in nature. However, many of these are crystallizable, especially while being oriented at high temperatures. Stretching at high temperatures, despite practical problems, is a desirable feature since maximum orientation is needed for ensuring optimum properties. The less effective methods, such as treatment of fibres under high pressure steam, with solvents or solvent mixtures at 100°, etc. are also employed to improve the properties. The method generally used is stretching at higher temperatures under inert atmosphere as shown in Table 2.

The Nomex fibre retains its original tensile strength up to 250°C and is useful up to 300°C. The hetero-cyclic polyamide fibres are thermally more stable up to 400°C. If the fibres are to be used in air, heat ageing is done in air, the properties are retained up to 1-2 weeks. In general, they have high volume resistivity and high dielectric strength up to a fairly high temperature which makes them suitable for some special Nomex nylon papers[66]. In view of their excellent oxidation and chemical resistance, Nomex fibres are used in fabrics for high temperature protection. At 285°C, the fibre is ≈ 50% as strong as it is at room temperature and shows similar retention of modulus. Its oxidation resistance makes it retain the original strength, even after exposure for 1000 hr at 260° and for 200 hr at 300°C. The fibre does not melt and ignites only with difficulty; as such it is self-extinguishing and hence is useful as a protective clothing. A similar use has been in the preparation of special type of Nomex nylon papers. The polyamide papers, like the fibres, neither melt nor burn independently. The tensile strength of the paper decreases gradually with temperature and at 225°C becomes 68% of the original value. In general, they have high volume resistivity (1·3 × 10^6 ohm cm) and high dielectric strength even at high temperatures. A major advantage of these papers is in heat sealable application and high temperature dielectrics for use in motors and trans-

formers. In view of its high flexural strength, Kevlar is used in the manufacture of bolting for high pressure hydraulic systems and material handling equipment. In comparison to steel and viscose rayon, Kevlar reinforced radial tyres give longer thread life for the least weight. Kevlar 29 is used in slings and strappings. It can be woven alone or together with other fibres to produce industrial fibres, balloon fabrics, coated fabrics, parachute fabrics, etc. A Kevlar polyester fibre sail cloth is used in racing yachts. These fabrics are used for the production of laminates and composites, which are used in interior and exterior parts in aircrafts[67]. These polyamide fabric laminates with epoxy polyester resin compositions increase the stiffness of boat hulls, paddles and spars and are 50% stiffer than typical glass reinforced plastics[68-70]. Considering the cost and performance, they stand in between glass and carbon fibres. The specific modulus is very high for Kevlar and the use of these fibres in place of a aluminium parts in aircraft reduces the weight by 40%.

Summary

Recent developments in various aromatic polyamides are reviewed with emphasis on their preparation, structure-property relationship and processability to convert them to suitable fibres. Latest trends in research on these fibres and their applications are also indicated.

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