

Aramid is an acronym originating from *aromatic poly(amide)*. Wholly aromatic poly(amide)s (PA)s were described in the 1960s [1–3]. Aramid fibers were originally intended to replace steel belting in vehicle tires. Aramids are reviewed in the literature [4–7].

In addition to wholly aromatic PAs, PAs are termed as aromatic PAs when at least one constituting component is of an aromatic nature [8]. These types of partially aromatic PAs are in between nylons and aramids. The particular advantages are easier techniques of polymerization and fabrication. So, if the properties of partially aromatic PAs are sufficient for certain particular applications they can be used instead of wholly aromatic PAs. Partially aromatic PAs are dealt with in this chapter only marginally; they are summarized in Chapter 12.

The functional properties of the aramid-reinforced composites have been reviewed [9]. These depend primarily on the properties of the aramid reinforcing fibers, since the fraction of the fiber constituent in the reinforced composites is quite high. The properties of the aramid fibers can be tailored by their chemical composition and manufacturing conditions.

## 13.1 Monomers

Monomers for poly(arylamide)s are shown in Table 13.1. As for nylons, the monomers are used as a combination of diamines and diacids, or derivatives of diacids, respectively. The acid groups are activated as they are converted into acid chlorides. The most common diacid chlorides are shown in Figure 13.1. Most common diamines are shown in Figure 13.2.

Wholly aromatic PAs based on 1,4-bis(4-carboxyphenoxy)naphthalene or 2,6-bis(4-carboxyphenoxy)naphthalene and aromatic diamines are readily soluble in a variety of organic solvents such as dimethylacetamide and *N*-methyl-2-pyrrolidone (NMP) [11, 14]. Naphthalene-based diacid monomers are shown in Figure 13.3. Transparent, tough, and flexible films of these polymers can be cast from the solutions.

5-Amino-2-(4-aminophenoxy)-pyridine is another type of diamine for organically soluble wholly

aromatic PAs [12]. The basic structure of the PA is not very much changed. Note that 5-amino-2-(4-aminophenoxy)-pyridine is very similar to 4,4'-diaminodiphenyl ether. Obviously, it is sufficient to introduce asymmetry into the molecule to achieve solubility. The thermal properties of the resulting aramids are essentially unchanged.

Polymers based on AB<sub>2</sub> types have been reported to be used in combination with bismaleimide polymers, in order to initiate curing [13]. Monomers for hyperbranched poly(arylamide)s are shown in Figure 13.4.

## 13.2 Polymerization and Fabrication

Aromatic polyamides are prepared via two major general routes [13]:

1. Polycondensation reaction via an aromatic diacid chloride and a diamine, and
2. Direct polycondensation reaction of a dicarboxylic acid and a diamine.

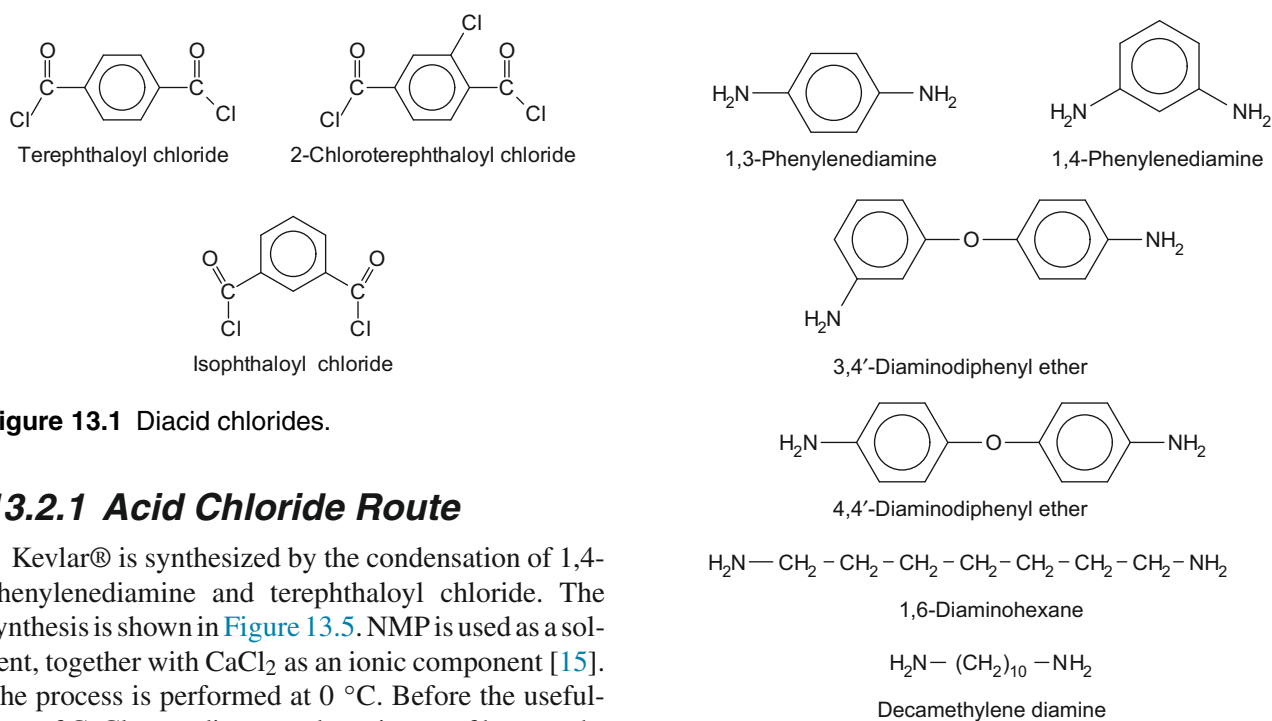
Furthermore, other routes have been suggested that seem to be used rather rarely.

For the first route, the polymerization is usually conducted at temperatures at or below 0 °C under an inert atmosphere. This is necessary, because of the extreme moisture sensitivity of diacid chlorides and the highly exothermic nature of the reaction between an amine and a carboxylic acid chloride. In order to achieve a high molecular weight for the resulting polyamides, the diacid chloride monomers must be purified prior to polymerization.

The dicarboxylic acid monomers used in the second route are cheaper, in comparison to the diacid chloride monomers. They are much less sensitive to moisture and relatively easy to purify via recrystallization. However, the condensation reaction proceeds badly under ambient temperature conditions. Therefore, a phosphorus-based promoter such as triphenyl phosphite is used to activate the carboxylic group and the reaction is conducted at elevated temperatures.

**Table 13.1** Monomers for Poly(arylamide)s

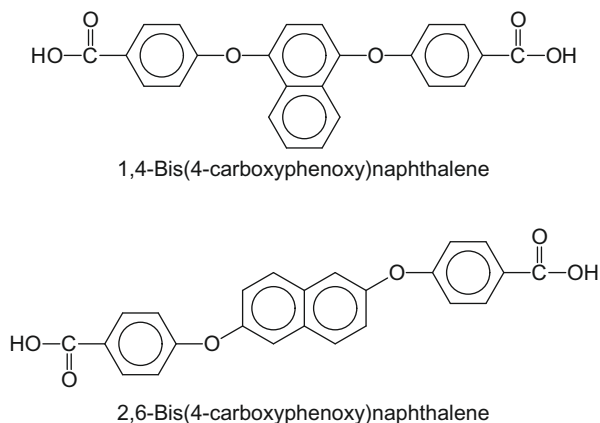
	Remarks
<i>Diamines</i>	
1,4-Phenylenediamine	Kevlar®, Twaron®
1,3-Phenylenediamine	Nomex®
3,4'-Diaminodiphenyl ether	Technora®
4,4'-Diaminodiphenyl ether	Films [10]
<i>Diacids</i>	
Terephthaloyl chloride	Kevlar®, Twaron®
Isophthaloyl chloride	
2-Chloroterephthaloyl chloride	Films [10]
1,4-Bis(4-carboxyphenoxy)naphthalene	Organically soluble [11]
2,6-Bis(4-carboxyphenoxy)naphthalene	Organically soluble [11]
5-Amino-2-(4-aminophenoxy)-pyridine	Organically soluble [12]
<i>AB<sub>2</sub> Types</i>	
2,3-Bis(4-aminophenyl)-quinoxaline-6-carboxylic acid	Hyperbranched polymers [13]
2,3-Bis(4-aminophenoxyphenyl)-quinoxaline-6-carboxylic acid	Hyperbranched polymers [13]

**Figure 13.1** Diacid chlorides.

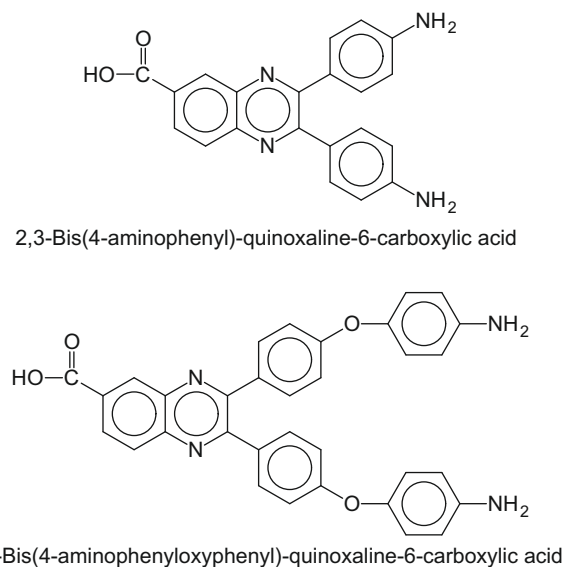
### 13.2.1 Acid Chloride Route

Kevlar® is synthesized by the condensation of 1,4-phenylenediamine and terephthaloyl chloride. The synthesis is shown in Figure 13.5. NMP is used as a solvent, together with  $\text{CaCl}_2$  as an ionic component [15]. The process is performed at 0 °C. Before the usefulness of  $\text{CaCl}_2$  was discovered, a mixture of hexamethylphosphoramide and NMP had been proposed [16].

**Figure 13.2** Diamines.



**Figure 13.3** Naphthalene-based diacid monomers [11].

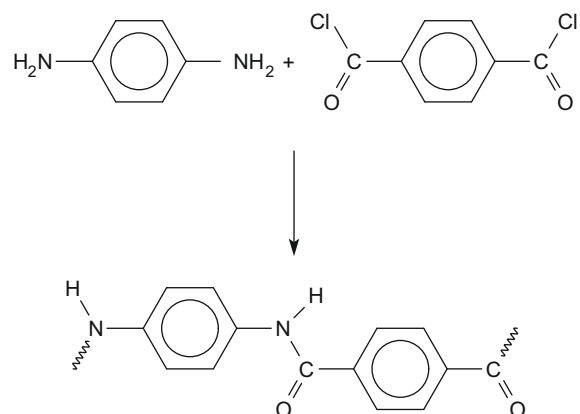


**Figure 13.4** Monomers for hyperbranched poly(arylamide)s [13].

### 13.2.2 Acid Route

The preparation of amides via the free acid, diamine and catalysts, is also referred to as the *Yamazaki* reaction [17]. Organic phosphor containing compounds, such as triphenyl phosphite, are used as catalysts. In addition, in NMP/pyridine solvents, salts such as LiCl and CaCl<sub>2</sub> are dissolved that favor polymerization.

The reaction has to be conducted at elevated temperatures in order to achieve high-molecular-weight polymers. Isophthalic acid gives somewhat higher molecular weight polymers than terephthalic acid. Nevertheless, for certain types of PAs, products with



**Figure 13.5** Synthesis of aramids from diamines and dichlorides.

only low molecular weights are obtained [18]. The acid route is used primarily for the preparation of specialized types of polyamides.

### 13.2.3 Carbon Monoxide Route

As pointed out already above, aromatic polyamides are conventionally prepared by condensing aromatic diacid chlorides and aromatic diamines in polar aprotic solvents. A disadvantage of such a process is that the variety of aromatic polyamides produced is limited by the small number of commercially available diacid chlorides. Moreover, the diacid chlorides are hydrolytically sensitive.

A process that uses carbon monoxide, an aromatic dichloride, and a diamine has been suggested. A palladium complex bis(triphenylphosphine) palladium(II)chloride is used as catalyst that induces the carbonylation of aryl aromatic chlorides [19].

### 13.2.4 Partially Aromatic Poly(amide)s

Partially aromatic polyamides consist of aromatic dicarboxylic acid and aliphatic diamine monomer units. Such polyamides are generally characterized by high melting points, high glass transition temperatures, low moisture absorption and, unlike aliphatic polyamides such as nylon 6 and nylon 66, good dimensional stability under moist conditions.

The combination of high temperature and dimensional stability renders partially aromatic polyamides particularly suitable for use in electronics, engineering plastics, films, and fibers [20].

Partially aromatic PAs can be prepared from the acid, instead of the acid chloride in a multi-step process. The first steps are conducted as a solid state polymerization with increasing temperature steps, and optionally feeding monomers after each reaction step. The final steps are proceeding as a melt condensation reaction [8].

Alternatively, instead of the acids, the corresponding esters can be used as starting materials [20]. Esterification of the dicarboxylic acid advantageously lowers its melting point to a temperature that allows melting of the acid while minimizing the thermal degradation. The admixture of the dicarboxylic acid component and the diamine component in the form of a melt is thereby facilitated.

Further, the partially aromatic polyamide formed by these reactants likewise contains alkyl side chains that also depress the melting point of the final PA. Thus the resulting PA can be more readily processed than the corresponding polyamide that lacks such alkyl side chains.

### 13.2.5 Fibers

Fibers are delivered in three basic forms:

1. Continuous multi-filament yarn,
2. Staple fibers (cut and crimped), and
3. Pulp (short cut and fibrillated).

#### 13.2.5.1 Spinning

Aramid fibers have been reviewed in the literature [5,21]. The conventional aromatic PAs suffer from being insoluble in organic solvents. Therefore, for Kevlar®, fiber spinning is done in concentrated sulfuric acid as a solvent. The spinning mass used is prepared by mixing sulfuric acid with the polymer at 70–100 °C [22,23].

In air gap spinning, aramid solution is forced through a spinneret whose face is in contact only with a gas, usually air. After traveling a short distance through the air, the solution enters a coagulant in the form of a fine jet.

The coagulant extracts the solvent from the polymer, resulting in the formation of the polymer fiber [24]. The coagulant is water. The addition of small amounts of a drag reducing polymer allows a higher throughput or the production of fibers with

a smaller diameter. Poly(ethylene oxide) is a suitable drag reducer.

Aramid nanofibers have been prepared by an electrospinning technology [25]. The addition of LiCl plays an important role both for helping dissolving and in electrospinning because the electrical conductivity of the solution increases. These nanofibers can selectively absorb certain materials. For example, aramid nanofibers can be used to effectively remove endocrine disruptors such as bisphenol A, phenol, and *p*-hydroquinone from their aqueous solutions. Also, the nanofibers can be used in molecularly imprinted technology.

Bulk aramid macroscale fibers can be effectively split into aramid nanofibers by dissolution in dimethyl sulfoxide under alkaline conditions. Also aramid nanofiber-functionalized graphene sheets can be prepared by adding a graphene oxide dispersion to a nanofiber solution in dimethyl sulfoxide and reducing with hydrazine hydrate [26]. The nanofibers are then absorbed on the surface of the graphene nanosheets and can be easily exfoliated and dispersed in *N*-methyl-2-pyrrolidone. A combination of these two ultra-strong materials can be used as nanofillers for the reinforcement of polymers. Improved thermal stability and UV-shielding are observed.

Scanning electron microscope images show that the carbon nanotubes are well dispersed in the composite films and are wrapped with *m*-aramid chains [27]. Further, the interfacial thickness of the aramid wrapped carbon nanotubes decreases with their content.

Therefore, the maximum temperature that can be reached at a given applied voltage can be controlled by the amount of carbon additive. The films exhibit an excellent electric heating performance as a rapid temperature response occurs and a high electric power efficiency at voltages of 1–100 V is observed [28].

The adhesion of aramid fiber composites can be improved by a core/shell structure of meta-aramid/epoxy nanofibers [29]. The polymer blends are prepared by electrospinning to enhance the interface adhesion.

Aramid polymers useful for spinning fiber can be obtained by the reaction of a diamine with a diacid chloride in solution. This reaction produces hydrochloric acid as a byproduct, which can be neutralized by the addition of a basic compound to form a salt [30]. Fibers are then spun from this solution and the solvent must be removed from the fiber during its

initial formation. Subsequent steps are then employed to remove as much solvent from the fibers as possible and draw the fiber to develop improved fiber physical properties.

The process for fiber manufacture has been physically separated or decoupled into two isolated steps, the first for spinning the fiber, operating at a high rate or speed. Then a subsequent slow rate or speed washing and drawing process is done. This process runs rather slow. Therefore a method for the rapid removal of the solvent from the fiber after spinning has been proposed.

A continuous dry spinning process has been developed where a solution of polymer, water, and salt is extruded into a gaseous medium [30]. The gaseous medium removes at least 25% weight percent of the solvent from the fiber. Then the fiber is quenched in an aqueous solution. After the fiber is conditioned, the fiber is eventually drawn.

A method for the production of aramid fibers has been described that results in fibers with a high surface uniformity and improved tensile strength [31]. In particular, the surface uniformity can be improved by an optimized spinning, thereby resulting in improved tensile strength and elongation properties.

A high-tenacity aramid yarn can be fabricated from a copolymer from 5-(6-amino-2-(*p*-aminophenyl)benzimidazole), *p*-phenylenediamine, and terephthaloyl dichloride [32]. Also, 2-chloro-*p*-phenylenediamine and 2-chloroterephthaloyl dichloride can be used.

The yarn is heated in at least two process steps. In the first step, the yarn is heated to a temperature of 240–330 °C at a tension of at least 0.2 cN dtex<sup>-1</sup>. In the second step, the yarn is heated at a temperature of 400–470 °C at a tension of less than 1 cN dtex<sup>-1</sup>.

The highest increase of the tenacity in comparison to the conventional one-step method is obtained, when the copolymer is made from a mixture of monomers, wherein 12.5–17 mol% is 5-(6-amino-2-(*p*-aminophenyl)benzimidazole) [32].

### 13.2.5.2 Modification and Treatment

Fabric blends of aramid fibers and flame-resistant cellulosic fibers have been described. These fabric blends are popular for use in protective garments and are more comfortable than fabrics made of aramid fibers alone [33].

*p*-Aramid fiber has a highly ordered fibrillar structure with a propensity for fibrillation attributable to the lack of lateral forces between macromolecules. As the *p*-aramid content of a fabric increases above 5%, the extent of fibrillation of the *p*-aramid fibers increases and the actual fibrillations can become more noticeable and objectionable. With the wear, abrasion and laundering that occurs as the fabric article is used over time, fabrics lose their esthetic appeal.

The appearance of the fabric can be restored by a dye treatment. Highly fibrillated areas of cloth can be placed in an aqueous bath at Basic Yellow 40. The materials are contacted with the aqueous dye solution for 30 min followed by a treatment of a 10% detergent solution of hexylene glycol at 60 °C for 10 min. Finally, the materials are rinsed thoroughly with water and dried [34].

Hydrophobically finished aramid fabric can be produced by a water-repellant agent. In addition, the application of an antistatic agent is advantageous [35]. The water-repellant agent is a mixture of fluoroacrylate polymers.

### 13.2.6 Aramid Paper

Aramid paper pulp may consist both of the meta and the para forms of aramid. Short fibers, staple fibers, pulp, and polymer particles of aramid swollen with water can be used as starting material for aramid paper. Papermaking is done in a conventional manner.

Aramid paper pulp can contain both aramid floc and aramid fibers. Flocs are addressed as short fibers cut from longer aramid fibers. High porosity papers can be made using high levels of floc instead of fibers [36].

Alkaline treatment of the pulp results in papers with enhanced tensile strength [37]. It is believed that the alkaline treatment effects hydrolysis reaction of the surface of the polymer. Thus the surface contains an increased amount of amino groups. These materials can be used in slipping clutches.

Aramid pulp is widely used as a substitute for asbestos [38]. The aramid paper is used as insulating paper. In this case, mica, ground quartz, glass fibers, alumina, or talc, can be incorporated to improve the insulating properties. In contrast, if alumina laminae, carbon black, or stainless steel short fibers are incorporated, electrical conductive papers are obtained. Aramid paper is also used as a reinforcing agent in honeycombs.

A nanocomposite paper based on aramid nanofibers and graphene oxide has been described that is fabricated by a vacuum-assisted filtration followed by reduction [39]. The nanocomposite paper is mechanically robust and electrically conductive.

Further, aramid paper is less hygroscopic than cellulose paper [40]. However, a poly(ether imide) paper absorbs less water than a conventional aramid paper [41]. Therefore, especially under humid conditions, a poly(ether imide) paper is superior to an aramid paper.

The length of the aramid fiber plays an important role on the adhesive properties and the strength of the paper [42].

The papermaking technique is an efficient procedure to fabricate non-woven membranes. A papermaking process can be used to fabricate aramid membranes. Here, aramid short fibers and aramid pulps are soaked with water and pulped to form a completely dispersed fiber suspension. Then a wet aramid sheet is made on a papermaking machine. These aramid membranes are suitable for lithium ion batteries [43]. The membranes have good electrolyte wettability, high ionic conductivity, excellent flame retardancy, and superior thermal resistance. In addition, such membranes exhibit stable charge/discharge profiles and a satisfactory cycling stability even at a temperature of 120 °C.

Pulp is a fiber stem which is highly fibrillated. The fibrillated part is addressed as fibrils, which are highly entangled and have a high aspect ratio of greater than 100 and a large surface area of 8–10 m<sup>2</sup> g<sup>-1</sup>. Aramid pulps are fibrillated particles that are used for making paper, gaskets, and breaking lines.

The pulp can be made from spun fiber, by performing cutting and fibrillation steps thereon. However, it is advantageous to directly make pulp, without first spinning the polymer to a fiber [44].

Aramid paper laminates can be formed by calendering the opposing surfaces of the aramid paper at different temperatures prior to laminate formation [45]. Laminates made from aramid paper laminates are useful in electrical transformers, wherein the laminate serves as a dielectric insulation material.

An electroconductive aramid paper can be made by the addition of a conductive filler, such as carbon fiber [46]. The paper should also have a certain level of surface resistivity to avoid the buildup of charge and provide an optimum electrical shielding.

A strong paper with no significant changes in the paper free volume or surface resistivity can be made by heat-treating the formed paper at a temperature of

about or above the glass transition temperature of the polymer, however, without applying substantial pressure to the sheet in the heated state to consolidate or compress the paper [46].

An aramid insulating paper with enhanced strength, smoothness, and uniformity can be prepared by [47]:

- Providing aramid pulp slurry and aramid short fiber slurry at respective desired concentrations,
- Blending, beating, and fluffing the aramid pulp slurry and the aramid short fiber slurry in a given ratio to afford a paper pulp at a desired concentration,
- Transiting the paper pulp to a papermaking machine fitted with a head box to form and make wet paper sheets,
- Pressing to dewater the wet paper sheets and drying the dewatered paper sheets, and
- Calendering the dried paper sheets at a high temperature to obtain the desired aramid insulating paper.

The dispersion and flocculation of the paper pulp may seriously affect the mechanical strength and uniformity of the aramid insulating papers, and the degree of orientation of the short fibers also has a great impact on the mechanical strength of the aramid insulating papers. These drawbacks can be solved by utilizing ultrasonic waves in the papermaking process [47]. The ultrasonic waves are applied to the paper pulp so as to boost the dispersion of the aramid short fibers, substantially decrease the amount of degree of vertical orientation of the short fibers, and increase the amount of degree of horizontal orientation of the short fibers along the flow direction.

An aramid polymer can be crosslinked in the presence of polymers from acrylic acid or methacrylic acid [48]. The crosslinked polymer is obtained by polymerizing a monomeric aromatic diamine with a monomeric aromatic diacid in the presence of poly(meth) acrylic acid, followed by a curing step. The curing step is simply a thermal curing. The crosslinked aramid polymer is then crosslinked via its amide bonds. Here it is not necessary to modify the aramid backbone with other monomers.

Previously, as the crosslinking agent a modified aramid copolymer having at least two aromatic hydroxyl groups, polyvinyl alcohol, and an aromatic hydroxyl group containing monomer was used [49].

### 13.2.7 Honeycombs

Aramid honeycombs find use in the fields of aerospace, transport equipment, etc. Aramid honeycomb sheets comprising a nylon-type resin, particularly a *p*-aramid honeycomb resin, have flame retardant, tough, and other excellent properties required for a honeycomb core structure. However, the method of fabrication of aramid honeycombs is a rather complicated process. The process is described in detail in the literature [50,51].

### 13.2.8 Aramid Films

Aromatic PA films are produced by casting a polymer solution in sulfuric acid onto an endless belt. In addition, the solution contains microparticles of silica to improve the surface properties. The casting solution is guided after intermediate heating into a coagulation bath and the film is released from the belt and post-treated [52].

It is possible to condense the aramide directly in an NMP solution and cast the solution. This process directly produces a transparent film from an aromatic polyamide dope without requiring the step of dissolving the aromatic polyamide in concentrated sulfuric acid. The process does not require any acid-resistant equipment and is inexpensive [53].

A procedure for the production of a film has been reported as follows [10]: In NMP, 0.85 mol 2-chloro-*p*-phenylenediamine, and 0.15 mol 4,4'-diaminodiphenyl ether are dissolved. 0.985 mol 2-chloroterephthaloyl chloride is added. After 2 h, the polymerization is complete. The mixture is then neutralized with lithium hydroxide. The polymer solution is filtered and cast onto an endless belt. The solvent is evaporated at 160 °C. A film with a polymer content of 45% can be continuously peeled off from the belt. Then the film was guided into a bath of NMP and water to extract the residual solvent, the inorganic salt, and impurities. The film is stretched between nip rollers in the longitudinal direction at a stretching ratio of 1.20.

Applications of the films are in:

- Magnetic recording media,
- Acoustic diaphragms for audio speakers, and in
- Electronic applications.

Aramid-titania hybrid films have been prepared by the sol-gel technology [54]. The titania network can

be generated in situ by the hydrolysis and condensation of tetraethyl ortho-titanate [55]. 3-Isocyanatopropyltriethoxysilane was added to strengthen the bonding of the titania to the polymer backbone and lessen the agglomeration of titania. The thermal degradation of these materials at 450 °C in air resulted in uniformly agglomerated rod-like anatase nanoparticles [54].

Aramid nanocomposite films with 1% hybrid fillers of graphene and multi-walled carbon nanotubes have been prepared by solution casting [28]. The electric heating behavior has been investigated as a function of the composition of the carbon fillers. The electrical resistivity can be controlled by the amount of graphene and carbon nanotubes added.

### 13.2.9 Nanocomposites

Conventionally, nanocomposites are restricted to a somewhat limited set of building blocks, some of them with a low reactivity. This drawback has been overcome by the creation of functionalized nanometer-scale aramid structures, both as nanofibers and nanosheets [56]. Such compositions can be obtained by deprotonating Kevlar yarns by potassium hydroxide in dimethyl sulfoxide. In this way, stable dispersions of nanometer-scale aramid fibers are obtained that can be further hydrolyzed with phosphoric acid.

So, a wide variety of nanostructured aramid materials with tailorable properties can be synthesized. For example, such functionally active nanostructures can be crosslinked by glutaraldehyde [56].

Aerogels are quasi-stable, low-density, three-dimensional assemblies of nanoparticles, which have usually poor mechanical properties. A facile one-pot synthesis of Kevlar-like aerogels based on the reaction of multifunctional isocyanates and carboxylic acids has been reported [57]. The materials exhibit an ultimate compressive strength, a high specific energy absorption, and a thermal conductivity like foamed PS. By a pyrolysis process at 800 °C, the materials can be converted to a porous, electrically conducting carbon with a high surface area.

Poly(methyl methacrylate)/aramid nanoblends have been developed [58]. In detail, aramid from 1,5-diaminonaphthalene and 1,3-phenylenediamine with terephthaloyl chloride is incorporated in poly(methyl methacrylate) to get nanostructured blends by physical interlocking. DSC studies indicated

completely miscible blends even at a high content of aramid.

Blends composed from pure poly(styrene) (PS) and amino-functionalized poly(styrene) and an aramide made from 1,5-diaminonaphthalene and 1,4-phenylenediamine with isophthaloyl chloride have been described [59]. The amino groups effect a remarkable cocontinuous self-assembled morphology.

## 13.3 Properties

Properties of an aramid fiber are shown in Table 13.2. Extensive tables of chemical stability are given in the literature [60]. Nomex® can be chlorinated without any significant decomposition, however, Kevlar® decomposes under the same conditions of chlorination. Experiments with model compounds revealed that the *p*-diaminophenylene moiety is oxidized to a quinone intermediate when treated with hypochlorous acid, that is not stable. In contrast, with Nomex® such a reaction mechanism is not possible [61].

### 13.3.1 Mechanical Properties

The tensile strength of aramids is comparable to that of cast metals. In addition, they exhibit low creep and low water absorption. Therefore, these materials are suitable for metal replacement.

In the case of high loading rates, an increase in material stiffness and strength compared to the static

behavior may occur. This is addressed as strain rate effect. This effect is important in dynamic finite element calculations. Actually, by taking account of this effect the material may be designed more lightly. A strain rate effect has been demonstrated for aramid paper honeycombs [62].

#### 13.3.1.1 Friction and Wear Properties

Aramid-containing composites are often used in sliding applications. The estimation and prediction of the tribological properties of such composites is a desirable skill. Despite the increasing use of polymeric composites, the knowledge of their tribological behavior is limited and lacks predictability.

Studies with a pin-on-disk apparatus have been performed to elucidate the tribological behavior of aramid-containing polymer composites. These studies include theoretical considerations and can serve as a directive on how to get information about tribological and wear properties in other related systems [63].

The effect of ultra-high molecular weight poly(ethylene) (UHMWPE) on the mechanical and solid particle erosive wear behavior of aramid fabric reinforced-epoxy composites has been investigated [64]. A silica sand of a size of 150–280  $\mu\text{m}$  was used as an erodent. The erosive wear rate of UHMWPE in aramid-epoxy composite exhibits a lower value in comparison to neat composites. A maximum erosion rate was observed at an impingement angle 60°, and the material behaves in a semiductile manner.

The effect of a surface treatment with epoxy compounds on aramid yarn laminate composites was investigated [65]. An optimum level of amount of epoxy could be identified. By increasing the twisting of the yarn up to an optimum level, the tensile strength of fiber bundle as well as tensile and bending strength of the composite increases. However, the interfacial properties of composites with various twisting levels do not change.

#### 13.3.1.2 Impact Behavior Properties

Impact problems are becoming increasingly important to industry, with respect to safety issues. The designer has to take into account accidental loads of the material caused by dropped objects, collisions, or explosions. Particularly with respect to aramid materials, ballistic protection applications are an important issue. Advantageously, the materials should have a large capacity to absorb kinetic energy.

**Table 13.2** Properties of an Aramid Fiber<sup>a</sup> [60]

Property	Value	Unit
Density	1.44	$\text{g cm}^{-3}$
<i>Straight test on conditioned yarns</i>		
Tensile modulus	70,500	MPa
Elongation break	3.6	%
Breaking tenacity	2900	MPa
Specific heat (25 °C)	1.42	$\text{J kg}^{-1} \text{K}^{-1}$
Thermal conductivity	0.04	$\text{W m}^{-1} \text{K}^{-1}$
Decomposition temperature (air)	427–482	°C

<sup>a</sup> Kevlar™ 29, DuPont.



There are standard test methods for testing the impact strength under ordinary conditions [66,67]. In addition, there is an ISO Standard with respect to bullet resistance of protective clothing [68], but remarkably there is no ASTM Standard with respect to this topic.

In classical ballistic tests, a projectile is shot at a stationary target that consists of the material to be tested. The residual kinetic energies are studied. A recently developed technique for lightweight materials uses the reverse ballistic impact. In contrast to the classical tests, the target is moving and the projectile is at rest [69]. Nitrogen from a commercially compressed gas bottle can be used as acceleration gas. Velocities of up to  $400 \text{ m s}^{-1}$  can be achieved, depending on the nature and the pressure of the gas.

As an exemplary result of the study retain, it has been found that in comparison to standard shooting tests with soft bullets, woven aramid panels have a slightly better resistance than knitted panels with a comparable areal density [69].

### 13.3.2 Thermal Properties

The high fluidity of aramids at elevated temperature enables fabricating thin parts by conventional injection molding techniques. The flow properties are retained even at a glass fiber content as high as 60%.

### 13.3.3 Optical Properties

Aramid is sensitive to UV light. The effects of simulated solar UV irradiation on the mechanical and structural properties of a poly(*p*-phenylene terephthalamide) fiber have been studied [70]. UV irradiation deteriorates the surface and defect areas of the fiber by photoinduced chain scission.

Tenacity, break extension, and energy to break of the filaments decrease rapidly and almost linearly. After 144 h of irradiation, the energy to break drops below 40% to the initial value. Oxidation of the end groups occurs in air. The crystalline structure remains nearly unchanged.

### 13.3.4 Wettability

The effect of the polyamide benzimidazole group on the surface wettability and interfacial adhesion of fiber/matrix composites of two kinds of aramid fibers from poly(*p*-phenylene terephthalamide) (Kevlar-49) and poly-(polyamide benzimidazole-*co-p*-phenylene terephthalamide) (DAFIII) have been

investigated [71]. The incorporation of the polyamide benzimidazole moiety effects more polar functional groups on the DAFIII surface. DAFIII has a larger rough surface in comparison to Kevlar-49 due to the different spinning processes used.

## 13.4 Special Additives

### 13.4.1 Ultraviolet Stabilizers

Aramid fibers have an inherently poor resistance to ultraviolet light. Thus, fabrics made from aramid fibers change in color when exposed to ultraviolet light. In addition, there is a significant loss of strength to the fabric. Ultraviolet absorbers or light screeners are often incorporated into the aramid fibers during manufacture or used to treat the aramid fibers in subsequent processing steps to improve their performance.

In the normal textile dye process, dye molecules typically penetrate the fiber and become entrapped therein. Alternatively, the dye molecules may chemically bond with the fiber. However, aramid fibers are difficult to dye using conventional techniques.

Thus, ultraviolet stabilization of aramid fibers is not easily accomplished by ultraviolet absorbers or light screeners in the dye bath. Actually, the normal dye process does not improve the ultraviolet stability of aramid fibers.

Textile pigment printing involves the printing of an insoluble coloring material on a textile fabric. The pigment, which has no affinity for the fibers of the fabric, is adhered to the fabric by a resin binder. It has been shown that a suitable pigment may serve as a UV stabilizer as such [72]. Resin binders are acrylic copolymer binders, styrene-butadiene latex binders, or modified nitrile polymer binders.

Tetrabutyl titanate was used as a sol-gel precursor of a nanosized  $\text{TiO}_2$  coating of aramid fibers. The photostability of the aramid fiber increased by this treatment [73].

### 13.4.2 Electrically Conductive Modifier

Often there is a need to drain or dissipate electrical charges off polymeric surfaces. Aramids are likely to collect electrical charges. Therefore, there is an inherent threat of sparking on discharge. Sulfonated poly(aniline) can be added to aramid in order to increase the electrical conductivity [74,75].

The electrically conductive composites prepared by these methods are not sufficiently conductive for shielding of electromagnetic interference. Still more effective in producing conductive aramids is electroless plating. A high electrically conductive fiber that is impregnated with metal complexes using supercritical carbon dioxide is obtained.

The metal complexes are activated by reduction in hydrogen and then immersed into an electroless plating solution. The process has been using palladium(II)-hexafluoroacetylacetonate. The palladium complex can be activated in the absence of hydrogen [76]. This reduces the risks of explosion in a technical process.

### 13.4.3 Peroxide Modified Aramid

Aramid particles that contain a peroxide as radical initiator can be used for the vulcanization of an elastomer [77]. Rubber with excellent hysteresis and heat buildup without other adverse effects are obtained.

## 13.5 Applications

Aramid fibers are notorious for their application in bulletproof jackets, more generally addressed as ballistic resistant fabric articles [78,79]. Less exciting applications of aramids are in automotive, electrical, and electronic fields. They are also used in medical devices. Specific uses are summarized in Table 13.3.

### 13.5.1 Friction Materials

For the formulation of friction materials, both powdery and fibrous materials are mixed together. The binder consists of phenolic resins. Alternative binders include melamine resins, epoxy resins, or poly(imide) resin.

Nowadays, in place of asbestos, fibrous reinforcements that include glass fiber, steel fiber, aramid fiber, potassium titanate fiber, etc., are used. Since these fibrous reinforcements have their own specific properties, in practice, a mixture of them is used [80]. Potassium titanate fiber is a hard inorganic fiber which can improve the strength, heat resistance, and wear resistance of the friction material. In addition, it can enhance the friction coefficient of the friction material through its abrasive property.

Friction modifiers include inorganic friction modifiers such as alumina, silica, magnesia, zirconia, chrome oxide, or quartz and organic friction modifiers

**Table 13.3** Fields of Uses for Aramids

Usage	Examples
Friction materials	Brake pads, linings, clutch facings
Gaskets	
Medical applications	Prosthetics, fibrous bone cement
Optical applications	Optical fiber cables
Papers	Insulating paper, friction paper
Protective applications	Fire-fighting, cut protection, ballistics
Reinforcing fibers	Tires, pipes
Ropes and cables	
Sporting equipment	Sail clothes, tennis strings

**Table 13.4** Components in a Friction Material [80]

Component	Amount (%)
Phenolic resin	10
Cashew dust	10
Barium sulfate	25
Zirconia	2
Graphite	8
Copper fiber	10
Aramid fiber	5
Potassium hexatitanate fiber	15
Potassium octatitanate fiber	15

such as synthetic rubber or cashew dust. Graphite or molybdenum disulfide serves as solid lubricants. Copper fiber increases the thermal conductivity of the formulation.

Typical components in a friction material are shown in Table 13.4. The formulations are cured at high

pressure and temperatures. It has been found out that potassium hexatitanate and potassium octatitanate fibers should be used together. In this way, the performance of the mixture can be increased considerably.

### 13.5.2 Gaskets

Gaskets and other seals are required for use in many applications where adjacent surfaces are to be sealed to prevent fluid or gas leakage [81]. Composite gasket materials made by a wet laid process are comprised of a fiber component which is distributed within an elastomeric binder matrix, together with property improving solid fillers [82].

The content of the fiber component is typically 3–15%. The elastomeric binder comprises about 3–15%. The rest are fillers. Aramids are used in fiber reinforced gaskets instead of asbestos fibers. Binders typically are synthetic rubbers. Typical components of a gasket formulation are shown in Table 13.5.

### 13.5.3 Reinforcing Materials

Aramid fibers are widely used as reinforcing fibers in high performance composites. One disadvantage is the poor adhesion to the matrix materials which arises from the lack of functional groups in the polymer [83]. To overcome the lack of adhesion, the fibers are treated by so-called finish formulations, which is essentially a surface treatment.

Aramid tire cords have been treated by argon plasma etching and plasma polymerization of acetylene. The combination of argon plasma etching and acetylene plasma polymerization results in a greatly improved pull-out force of 91 N in comparison to 34 N with the

untreated aramid tire cord. Thus, the plasma treatment improves the adhesion to rubber compounds [84].

A surface modification by plasma treatment, using oxygen as the treatment gas [85] has been reported. Immediately after the plasma treatment, the treated fibers exhibit lower water contact angles, higher surface oxygen and nitrogen contents, and larger interfacial shear strengths to epoxy resins. After aging, the fibers still retain their improved properties to some extent.

The effectiveness of such a finish can be tested by various methods, including [83]:

- Analysis of the composition of the surface with X-ray photoelectron spectroscopy,
- Contact angle measurements,
- Single-fiber pull-out tests, and
- Composite mechanical testing.

### 13.5.4 Catalyst Supports

Catalysts having inorganic supports are often heavy and awkward to deal with. They are generally in the form of small particles and have associated dust and fines. Such catalysts are often brittle or may become brittle in use. They may fracture or crumble causing increases in pressure drop or decreases in throughput of the chemical reaction that they are designed to facilitate.

A *p*-aramid polymer supporting a catalyst agent has been presented for several reactions [86]. The composition exhibits an improved catalytic activity in comparison to *m*-aramid polymer catalyst support. The actual catalyst agent is adhered on or within the support.

The technique of depositing or incorporating the catalyst agent or precursor of the catalyst agent onto the supporting polymer depends on the catalyst composition. Not all catalytically active materials can tolerate the conditions required to spin *p*-aramid polymer or to cast *p*-aramid polymer films. In these cases, it is preferred that the catalyst composition be made by depositing the desired catalyst agent or the precursor of the catalyst agent on the surface of the *p*-aramid polymer.

Examples of *p*-aramid supported catalysts are palladium catalysts for the dehydrohalogenation reaction and catalysts for the hydrogenation reaction of organic compounds.

**Table 13.5** Components of a Gasket Formulation [82]

Component	%
Aramid	7.6
Hydrogenated NBR	7.0
Calcium terephthalate	30.4
Kaolin	38
Other <sup>a</sup>	15
Phenolic resin	2

<sup>a</sup> Graphite, vermiculite, aluminum trihydrate, magnesium hydroxide.

### 13.5.5 Carbon Fiber Precursors

Poly(*m*-phenylene isophthalamide) (PMIA) and other aramids have been proposed as precursor for activated carbon materials [87]. These materials exhibit a very homogeneous micropore size. This property makes them usable as adsorbents, molecular sieves, catalysts, or electrodes.

PMIA-derived carbon fibers can be activated by carbon vapor deposition of benzene. The activated carbon fibers are suitable as molecular sieves for air separation [88]. Carbon fibers can be obtained from the aramid by pyrolysis at 750–850 °C. Which may take place in Ar or CO<sub>2</sub>.

The fiber may be pre-impregnated with H<sub>3</sub>PO<sub>4</sub>. Steam, CO<sub>2</sub>, and H<sub>3</sub>PO<sub>4</sub> serve as activators. The activation converts the amide groups in the polymer precursor into complex and heterogeneously distributed nitrogen functionalities [89].

Poly(*m*-phenylene isophthalamide) (PMIA) is one of the most important aromatic polyamides. It has been widely used because of its high thermal resistivity and its superior mechanical and electrical properties [90].

This aromatic polyamide can be synthesized by the solution polymerization of *m*-phenylenediamine with isophthaloyl chloride in a polar organic solvent, such as dimethylacetamide.

PMIA is resistant to high temperatures and is chemically stable. But its application as coatings and membranes is limited due to its poor interaction with other materials. A modification of PMIA with sodium methylsulfinylmethylide and 2-iodine-1-ethanol is helpful in this aspect [91].

The bonding properties between PMIA fibers and a corresponding pulp can be improved using silane coupling agents, modification by nitrification or phosphoric acid [92]. Aramid handsheets made from PMIA fibers that are treated with 20% phosphoric acid have the highest mechanical strength, and the tensile and tear strengths are higher than those of aramid handsheets made from untreated fibers. This arises, because the treated fiber surface has more oxygen moieties and has more roughness.

A nanofiltration membrane with PMIA, poly(vinyl pyrrolidone), and LiCl has been fabricated by a phase inversion technique [93]. The rejection of the PMIA nanofiltration membrane for the dyes Eriochrome black T, Eriochrome blue black B, and Alizarin red was all found to be more than 98% at 0.4 MPa. However, the rejection for NaCl was only around 5.5%. The flux increases largely with an increase of pressure and temperature, but the rejection for the dyes remains

over 99%. Thus, these membranes can be used for dye purification and desalination.

### 13.5.6 Nanofibrous Membranes

Aramid/poly(acylic acid) composite nanofibrous membranes with a diameter of 50–100 nm have been prepared by electrospinning [94]. The equilibrium adsorption capacity of 2,4-dichlorophenol on these nanofibrous membranes is 251.61 mg g<sup>-1</sup>. Acidic conditions favor the adsorption of 2,4-dichlorophenol. The adsorption behavior fits best the Freundlich isotherm model. The adsorption kinetics follows a pseudo-second-order model.

### 13.5.7 Cryogenic Fuel Tanks

Cryogenic fuel tanks are essential components for space transportation systems. Materials for cryogenic fuel tanks must safely carry pressure, external structural loads, resist leakage, and operate over an extremely wide temperature range. Aramids exhibit a wide range of service temperatures and are therefore candidates for such applications. A wide variety of skin and core materials have been tested for helium gas permeability [95]. It turned out that Nomex® is superior in comparison to Kevlar®. A low level of permeability could be achieved, which meets the requirements.

### 13.5.8 Workwear

Two workwears composed from either aramid or from a fire-resistant viscose/merino wool underwear and a viscose/aramid outerwear [96] were used for the study. The workwears showed no significant differences with respect to exhaustion, core temperature, and thermal comfort. However, the sweat distribution differed significantly in both workwears. For economic reasons, it has been suggested that the viscose/merino wool blended underwear favor the use of fire-resistant viscose blended fabrics in workwears.

### 13.5.9 Cut-Resistant Gloves

Cut-resistant gloves are fabricated from a cut-resistant composite yarn having a core yarn and a first wrapping yarn helically wrapped around the core yarn. The core is of 56–220 dtex glass fiber filament yarn. The first wrapping is a 110–680 dtex para-aramid yarn. An additional yarn is made from aliphatic polyamides or polyesters. Further, the lining yarn is a composite yarn of 110–560 dtex of an elastomer [97].

The cut-resistant composite yarn, the companion yarn, and the lining yarn are co-knit in the glove with the lining yarn plated on the interior of the glove and the cut-resistant composite yarn and companion yarn forming the exterior of the glove.

### 13.5.10 Hyperbranched Aramids

When monomers of the AB<sub>2</sub> types are used, hyperbranched polymers will be formed on polymerization [13]. The polymers can be employed to initiate bismaleimide polymerization. Another application of these polymers is to increase the toughness for thermosets such as bismaleimide polymers and epoxies.

### 13.5.11 Medical Applications

The delivery of therapeutic biomacromolecules, such as DNA or proteins that are taken up by endosomes may be hindered by the endosomal membrane. Actually, the endosomal membrane may protect the body against certain viruses. Anionic polymers that undergo conformational changes and become membrane disruptive in low-pH environments have the potential to assist in the delivery of these biomacromolecules across the endosomal membrane. Endosomolytic polymers can be synthesized by grafting

of some hydrophobic side chains to a poly(*L*-lysine isophthalamide) backbone [98].

## 13.6 Suppliers and Commercial Grades

Aramids are available in a variety of grades. These include:

- Glass fiber reinforced,
- Mineral filled,
- Flame retardant equipped, and
- Impact-modified types.

Fibers are delivered as pulps, which are chopped and refined fibers with a high surface area. The pulps are used as specialty additives that enhance performance by providing excellent reinforcement. Lightweight strength reinforcement can be achieved with continuous filaments. Honeycomb cores are available for aerospace industries. Spun yarn is used for protective coatings [99].

Suppliers and commercial grades are shown in Table 13.6. Aramid fibers are used for other uncountable matrix polymers as reinforcing fibers. These types

**Table 13.6** Examples of Commercially Available Poly(arylamide)s

Tradename	Producer	Remarks
Aramica®	Asahi	<i>p</i> -Aramid film
Armos®	Chimvolokno JSC	
Heracron®	Kolon Industries, Inc.	
Hydlar®	A. L. Hyde Co.	Reinforced aramid fiber
Ixef®	Solvay Advanced Polymers	
Kevlar®	Dupont	<i>p</i> -Aramid fiber
Mictron®	Toray Industries	<i>p</i> -Aramid film
Nomex®	DuPont	<i>m</i> -Aramid fiber
Rusar®	Termotex Co., Mytishchi [100, 101]	
Sulfron®	Teijin Chemicals	Sulfur modified aramid
Technora®	Teijin Chemicals	
Teijinconex®	Teijin Chemicals	<i>m</i> -Aramid fiber
Thermatex®	Difco Performance Fabrics, Inc.	Aramid and aramid blend fabrics
Twaron®	Teijin Twaron B.V.	

**Table 13.7** Tradenames in References

Tradename Description	Supplier
Amodel® 1000 Poly(phthalamide) [102]	Amoco Chemical Comp.
Apyeil® Meta-aramid fibers [30]	Unitika, Ltd.
Basofil® Melamine resin fiber [72]	BASF AG
Bayhydrol® Antistatic agent [49]	Bayer AG
Caprolan® Nylon 6 [78]	Shaw Industries
Carbowax® (Series) Poly(ethyleneoxide glycol) (PEG) [20]	Union Carbide Corp.
Chinfunex® Aramid 1313 Aramid fiber [30]	Guangdong Charming Chemical Co. Ltd.
Conex® <i>m</i> -Aramid [86,30]	Teijin
Cymel® (Series) Amino resins [49]	Cytec
Denacol EX-611 Sorbitol poly(glycidyl ether) [49]	Nagase Kaseikogyo K.K.
Kevlar® Aramid [50,72,78,86,49]	DuPont
Kraton® Styrenic block copolymer [78]	Shell
Luperox®331 M 80 1,1-Bis( <i>tert</i> -butyl-peroxy)cyclohexane solution [77]	Arkema
Nomex® <i>m</i> -Aramid [33,72,78,30,46]	DuPont
Polyox® 301 Poly(ethylene oxide) [24]	Union Carbide Corp.
Technora® Aramid [77,48,49,97]	Teijin Chemicals
Teijinconex® Aramid [77]	Teijin Chemicals
Trigonox® 29 1,1-Bis( <i>tert</i> -butylperoxy)-3,5,5-trimethylcyclohexane [77]	Akzo Nobel Polymer Chemicals
Twaron® Aramid [72,77,49,97]	Teijin Twaron B.V.

are not included in Table 13.6. Tradenames appearing in the references are shown in Table 13.7.

## 13.7 Safety

Inhalation toxicology studies with fibrils made from *p*-aramid have been documented [103]. Responses were detected, but the interpretation of these studies was regarded as controversial. There is some evidence for the biodegradability of *p*-aramid respirable-sized fiber-shaped particulates [104], the concept of which was supported in subsequent studies [105]. Actually, material safety data sheets report the possibility of lung injury, if fiber dust is inhaled for a prolonged time. On the other hand, aramids are not considered to be dangerous from skin contact or by ingestion.

## 13.8 Environmental Impact and Recycling

Traditionally, asbestos has been used in friction materials such as vehicle brake and clutch components because of its toughness and non-flammability. The use of asbestos has been restricted in many countries. Aramid, as an alternative material, has been increasingly used instead of asbestos. Aramid is a tough, synthetic fibrous material which is believed to be safer to health than asbestos.

Methods have been developed to differentiate between asbestos and aramid [106]. The method is based on rubbing a reference material against a sample of the unidentified material. The electrostatic charge produced at the rubbing location is then measured.

In order to develop a beneficial application for fly ashes, automotive brake lining friction composites have been developed. These are based on phenolic resin, aramid pulp, glass fiber, potassium titanate, graphite, aluminum fiber, and copper powder, in addition to fly ash [107].

### 13.8.1 Geotextiles

Aramid fibers, such as Twaron® fibers, have been proposed for their use as geotextiles for the reinforcement of alkaline ground. Their durability in such environments was studied by accelerated aging under alkaline conditions [108]. The lateral apparent crystallite size increases in the course of aging. Also, changes in the molecular weight have been evaluated by size-exclusion chromatography. The mass weight distribution gets somewhat narrower after aging.

### 13.8.2 Water Disinfection

Cellulose filters have been coated with aramid. Then, the coated filters were then chlorinated in a hypochlorite solution. The chlorinated and unchlorinated filters were checked for their ability to disinfect contaminated water. The chlorinated variant produced a reduction of  $10^5$  (5 log [109]) of *Escherichia coli* and *Staphylococcus aureus*, which was much higher than that observed on the unchlorinated aramid-coated cellulose filter [110].

Similarly, a poly(acrylonitrile)/*m*-Aramid hybrid composite exhibits a 7 log reduction against *E. coli* and *S. aureus* [111]. Also, *m*-Aramid/chitosan hybrid films are antimicrobial [112].

#### 13.8.2.1 Detoxification

Porous, permeable meta-aramid particles can be chlorinated or brominated to produce antimicrobial and detoxifying particles for their use in non-woven webs, paper, textiles, and many others [113]. The particles can be charged with halogen before or after incorporation into the respective application medium. The particles maybe also blends other polymers, such as cellulosic materials or poly(urethane). These particles are effective for the inactivation of pathogenic and odor-causing microorganisms and toxic chemical agents. The materials contain *N*-halamine units and exhibit a resistance to the degradation by ultraviolet light.

Antimicrobial *N*-halamine polymers and coatings have been recently reviewed [114].

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