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3,576,769

SEMICARBONIZATION OF THERMALLY STABLE AROMATIC POLYMERS

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11 Claims

ABSTRACT OF THE DISCLOSURE

Thermally stable aromatic polyamides in fiber or fabric form are subjected to a controlled heat treatment in air under moderate conditions, causing semi- or partial carbonization to occur, and the resulting fibers or fabrics are essentially non-flammable, thermally stable, chemically inert and exhibit good dimensional stability at elevated temperatures. Fibrous products obtained by this process are useful in temperature resistant composite structures and as protective covering for articles that may be exposed to flames.

BACKGROUND OF THE INVENTION

This invention relates to the preparation of dimensionally stable flame resistant aromatic polyamide fibers and fabrics using controlled heating in air to partially carbonize the fibers without destroying their flexibility and other desirable properties.

Elemental carbon exists in nature in various allotropic forms. The amorphous form of carbon is generally referred to as "carbon," whereas the crystalline forms are known as "graphite" and diamond.

Carbonized fibers were first produced by Thomas Edison in his search for incandescent conductive filaments. His original work was restricted to the carbonization of naturally occurring cellulosic materials, such as cotton and linen threads. Subsequently, cellulose was dissolved in zinc chloride and the polymer dopes spun into fibers which were then carbonized. Later, these carbonized fibers were further improved by deposition of carbon or graphite on the filaments (U.S. Pat. 248,416 T. Edison). With the development of flexible tungsten filaments, interest in these carbon filaments wavered.

In the late 1950's, however, a new interest arose in carbon fibers, due to a search for super-refractory materials for use in ablative composites. As a result, many patents and papers describing processes for the constructive thermal treatment of materials such as various types of rayon, cellulose and acetates have issued. A few of these are: (1) "Carbonization of Cellulose Fibers. I. Low Temperature Pyrolysis." M. Tang and R. Bacon. Carbon 2 (3) 211.1964; (2) "Carbonization of Cellulose Fibers II. Physical Property Study." R. Bacon and M. Tang. Carbon 2 (3) 221.1964; (3) "Electrically Conducting Fibrous Carbon." W. Soltes. U.S. Pat. 3,011,981, Dec. 5, 1961, (4) "Method for Carbonizing Fibers." W. Abbott, U.S. Pat. 3,053,775, Dec. 11, 1962, and (5) "Fibrous Graphite." C. Ford et al., U.S. Pat. 3,107,152, Oct. 15, 1963.

These patents and publications describe the preparation of essentially completely carbonized or graphitized fibers, in contrast to the organic fibers, rich in non-carbon elements, of this invention.

In recent years, many other polymer systems, such as for example, polyacrylonitrile, polybenzimidazole, polyvinylchloride, polyolefins and others have been used as precursors for the preparation of carbonized and graphitized fibers, using the techniques cited above or modifications thereof.

The two distinguishing differences between the process of the present invention and those of the prior art are

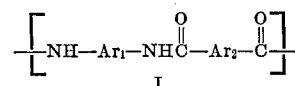
(1) the composition of the initial polymers and structures of the final products are radically different and (2) the products obtained by the process of the present invention are in the preoxidized or semicarbonized state, whereas the products of the numerous patents of the prior art are carbonized or graphitized. This is due to the fact that the conditions employed in this process are relatively moderate, in comparison to those used for carbonization and graphitization.

SUMMARY OF THE INVENTION

In general, the practice of the invention consists of heating thermally stable aromatic polyamide compositions, in the form of film, fibers, fabrics, webs or other shaped articles having a high surface to volume ratio, in air under carefully controlled conditions to transform the compositions into dimensionally stable, flexible, essentially non-flammable, chemically inert products. The time-temperature conditions of treatment are critical and dependent upon the polyamide having a threshold energy of activation for semicarbonization below the temperature at which loss of physical properties occurs, usually the softening temperature. If treated below a certain temperature, the desired transformation to the semicarbonized state will not occur and the product will burn on exposure to flames. If heated at too high a temperature or for too long a time in the optimum temperature range, the product will become too embrittled and weak. Satisfactory time and temperature conditions for most aromatic polyamides involve raising the temperature from room temperature (about 25° C.) to at least about 250° C. to 500° C. preferably during a period of from about 45 minutes to 1 hour. After reaching the maximum desired temperature the heat treatment is continued for less than one hour to about 12 hours to complete the transformation.

DETAILED DESCRIPTION AND PREFERRED EMBODIMENTS

The semicarbonization process of the invention is essentially a programmed time and temperature procedure with a fairly high degree of criticality. It is applicable to all types of thermally resistant wholly aromatic polyamide compositions. A "thermally resistant" polyamide is usually thought of as being one which has a melting point or decomposition temperature well in excess of polyhexamethylene adipamide (M.P. 268–270° C.) and ordinarily above 300° C. These aromatic polyamides, which are useful for carrying out the process described in this invention, may be generally characterized by the recurring structural unit.



wherein Ar₁ and Ar₂ are divalent aromatic ring nuclei in which the chain extending bonds connecting Ar₁ and Ar₂ to nitrogen atoms and carboxyl groups respectively are attached to non-adjacent carbon atoms. The term "aromatic ring" as used herein is intended to refer to any "aromatic ring system" which is of the arylene or heterocyclic type. The term arylene refers to single, multiple and fused ring residues, such as phenylene, biphenylene, and naphthalene.

A preferred method for the preparation of these polymer compositions is by means of the reaction of an aromatic diamine with an aromatic diacid chloride, as described in numerous patents and publications. The class of polymers of this type structure are those disclosed in U.S. Pats. 3,063,966, 3,232,910, and 3,232,213. As typical examples of such aromatic polyamides there may be mentioned poly-m-phenylenebis(m-aminobenzamido) terephthalamide, the polyterephthalamide of 4,4'-bis(4-aminobenzamido)diphenyl ether, poly-m-phenylene isophthalamide, poly-m-phenylenebis(m-aminobenzamido) 2,6-naphthylene dicarbonamide, poly-4,4'-diaminobenzanilide terephthalamide and the like. These aromatic polyamides are converted to the "semicarbonized" state, which essentially means a darkening in color coupled with an increase in carbon content but not approaching pure carbon. The carbon content of the final product is less than 90% weight of the composition and may be as low as about 70% or less depending on the starting composition.

Conversion to the semicarbonized state is most easily accomplished when the polymer is in a form which permits easy and rapid heat penetration, as well as facile diffusion of the oxidative reactant into the polymer. Obviously, a fiber is easier to treat uniformly throughout than a solid block of polymer. Thus, it is preferred that the polymer be in a form having a high surface to volume ratio such as fiber, film, fabric, web, cellular or other similar shaped articles. In addition, a gradual or programmed temperature increase is sometimes necessary in order to preclude the sudden violet evolution of off-gases which disrupts structural integrity or to allow reaction to begin gradually. This raises the melting point permitting still further reaction. The temperature range to which each polymer composition of this invention must be subjected has practical upper and lower limits. In particular, the threshold energy of activation for semicarbonization must be below the temperature at which major loss of physical properties occurs, while for reasons of practicality the reaction should proceed at a reasonable rate.

Although the exact mechanisms of the reactions responsible for the transformation that takes place within the polymer during the process are not fully understood, in all probability, they consist at least in part of hydrogen abstraction by oxygen, following by coupling of the residual radicals thus formed, to give ring formation and crosslinking. In addition to the reactions resulting in the desired transformation, it is also possible for other destructive thermal degradation reactions to occur which result in the breakdown of the polymer with loss of physical structure and properties. These must be minimized by choosing the proper reaction conditions.

In order that the desired transformation reactions take place without substantial change in the physical structure of the polymer, it is a necessary prerequisite that these reactions begin and progress to a substantial extent at a temperature below the temperature at which structural identity and usable physical properties are lost. Or, expressed in another way, the threshold energy of activation values for the desired reactions must be reached at a temperature below that at which coalescing of filaments, fusion of adjacent bodies or severe embrittlement occur. On the other hand, if the polymer softens, or detrimental changes in physical structure occur at a temperature below that which the desired reactions can take place (due to the fact that the activation energy values for the desired reactions are not reached); other reactions leading to chain scission and polymer degradation are likely to occur in preference to the transformation reactions. In this case, the textile structure of the fibers and fabrics will be lost or so weakened during the processes as to render the products obtained of little practical use. This invention, therefore, is primarily concerned with those polymers having a softening point above the temperature at which

desired transformation reactions begin. The term "softening point" as used herein refers to the temperature at which loss of physical properties occurs as indicated by differential thermal analysis melting point. The strong inflection observed is an indication of the softening temperature of the polymer and signals a major loss of some if not all physical properties in spite of the fact that structural identity may sometimes be retained until higher temperatures are reached or external stresses applied.

The invention is further illustrated by the following examples in which all parts and percents are by weight unless otherwise indicated.

EXAMPLE I

A sample of fabric prepared from poly-m-phenylenebis(m-benzamido) terephthalamide (PMPPT) was placed in a circulating air electric oven at room temperature. The fabric was allowed to hang free in order to allow unimpeded shrinkage. The oven temperature was raised to 420° C. during a 55 minute period and maintained at 420° C. $\pm$ 3° C. for two hours. The oven was shut off and as soon as the heat had diminished sufficiently to allow handling, the sample was removed. An elemental analysis of the starting material, the semicarbonized material, and the theoretical values for the polymer repeat unit, are listed in Table I.

TABLE I

	Sample			
	Percent C	Percent H	Percent N	Percent
Theory for repeating unit.....	70.58	4.23	11.76	13.43
Starting fabric.....	70.30	4.64	11.80	13.21
Semicarbonized fabric.....	69.95	3.18	12.99	12.76

From the above results, it can be seen that very little change in the carbon content of the sample occurred during this heat treatment, nor has the total chemical analysis been radically changed. The concentration of non-carbon material in the final product is essentially the same as that of the starting material. This is in marked contrast to the results obtained using the conventional techniques reported in the literature. These techniques involve the use of much higher temperatures and the resulting fibrous materials are essentially all carbon (i.e. 96% or greater) regardless of the starting material.

X-ray diffraction patterns of these semicarbonized yarns showed no evidence of residual orientation or crystallinity in the product. Microscopic examination of the cross-sections of several carbonized yarn samples, heat treated under approximately the same conditions as described above showed that darkening occurred uniformly throughout the filaments; there was no evidence of the formation of a carbonized sheath.

EXAMPLE II

A sample of fabric prepared from PMPBT yarn was heated in an air oven for 2 hours at 420° C. The resulting carbon-like product was quite flexible and exhibited 23.6% of the breaking strength of the original fabric. On exposure to the flames of a Meker burner, the fabric glowed red, and remained dimensionally stable.

EXAMPLE III

The effect of carbonization time of 400° C. on the percent shrinkage, percent weight loss, and breaking strength was determined using a sample of plain weave fabric (51 ends, 46 picks, 2-ply yarn, 180 total denier; 90 filaments/ply tape). The results of this series of runs are tabulated in Table II and show a definite loss pattern. From these results, it can be seen that most of the breaking strength loss occurs during the first two hours of treatment; however, further heating does cause additional strength, weight loss and reduction in product breaking strength.

TABLE II.—EFFECT OF TIME ON SEMICARBONIZATION OF PMPBT FABRIC (TAPE) AT 400°C.

Exposure time (hrs.):	Length (in.)	Fabric percent shrinkage	percent wt. loss	Breaking strength (lbs./in.)
0	12	0	0	174.4
2	10 $\frac{7}{8}$	9.3	20.25	14.8
2.5	10 $\frac{1}{2}$	12.0	27.92	10.7
3.0	10 $\frac{1}{4}$	14.6	35.75	10.0
3.5	9 $\frac{3}{4}$	17.2	43.41	11.4
4.0	9 $\frac{1}{2}$	17.7	49.34	7.75
4.5	9 $\frac{1}{4}$	21.4	55.97	8.15
5.0	9 $\frac{1}{8}$	22.4	58.42	7.9

EXAMPLE IV

Semicarbonization of a plain weave PMPBT fabric (34 pick count) was carried out under conditions believed to be near optimum for this composition (i.e. 55 min. room temperature to 420° C., two hours at 420° C.), as a result of preliminary experiments. A flexible nonflammable fabric was obtained which had a breaking strength retention of 16.1% in the warp direction and 11.5% in the fill direction. The tensile properties of the semicarbonized and untreated (control) fabrics are listed in Table III.

TABLE III.—TENSILE PROPERTIES* OF SEMICARBONIZED AND UNTREATED PMPBT FABRIC SAMPLES

	B. S. (lbs./in.)	Percent Elongation
Untreated:		
Wrap (42 ends/in.)	151.5	30.9
Fill (34 picks/in.)	122.0	19.5
Semicarbonized:		
Wrap (46 ends/in.)	24.4	8.4
Fill (38 picks/in.)	14.0	4.8

*Measured on $\frac{1}{2}$ " wide fabric strips in an Instron instrument at std. conds., 2" gauge, 100% ext./min.

EXAMPLE V

Preliminary semicarbonization tests had shown that the flammability of the carbonized yarn or fabric decreased with an increase in semicarbonization time. Flame tests were run on a series of close woven PMPBT fabric samples (tapes) that had been exposed to varying time-temperature semicarbonization conditions. The relative flammability and dimensional instability of samples exposed for less than two hours at temperatures of 400° C. or less and for longer periods of time at much lower temperatures were found to be excessive. The time could not be shortened to less than two hours by increasing the temperatures to 435° C. or above due to excessive thermal decomposition. The following observations will confirm the above statements.

- (a) A sample of PMPBT tape was thrust into a Meker burner flame. The tape instantly caught fire, melted and the fabric structure was destroyed.

- (b) A sample of the tape was heated in the air oven at 360° C. for 6 hours. The tape became dark brown. On exposure to flames, the tape caught fire.
- (c) A sample of the tape was heated at 390–400° C. for 1 hour, 45 min. On exposure to flame, excessive flash-off occurred and the fabric came apart.
- (d) A sample was heated for 10–15 minutes in air at 435° C. The tape although non-flammable, was excessively brittle and weak (i.e. came apart on flexing).
- (e) Heat treatment of a sample of tape at 505° C. for 10 minutes reduced the sample to an ash.

EXAMPLE VI

Elevated temperature breaks were run on a sample of PMPBT tape, which had been semicarbonized under near

optimum conditions. The breaks were made on an Instron instrument equipped with an oven for maintaining the desired temperature. The semicarbonized tape retained better than 50% of its room temperature breaking strength at 450° C.; and better than 30% at 500° C. These results demonstrate the dimensional stability of these products.

EXAMPLE VII

The preceding examples describe the heat treatment of fabrics (or tapes) in the air oven. Yarn samples were also heat treated while mounted in an Instron instrument. Using this instrument, it was possible to measure the shrinkage and stresses developed during partial carbonization of the yarn samples. The results obtained using PMPBT have shown that the tensile property changes associated with carbonization begin to take place at 400–420° C., and the minimum stress should be applied to a yarn during this phase of the heat treatment, if broken filaments are to be avoided. The following values represent typical physical properties of two unwoven PMPBT samples before and after semicarbonization.

	Treated	Semicarbonization	In Instron
25 Tension (g.p.d.)	4.86–5.68	2.03–3.1	0.4
Elongation percent	25.1–23.6	3.4–4.5	
Mi (g.p.d.)	83–105	89–127	

EXAMPLE VIII

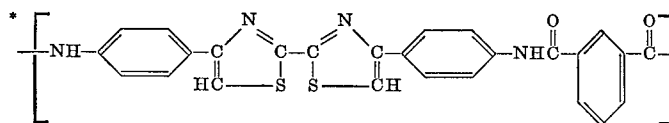
- 30 Yarn samples of PMPBT, semicarbonized PMPBT, and poly (m-phenyleneisophthalamide) were heated under minimum stress on a hot shoe surface to determine a measure of the shrinkage which occurred as a function of temperature from room temperature to 500° C. The semicarbonized yarn had a dry heat shrinkage of about 5% at 500° C.; whereas the untreated yarn had a shrinkage of about 30% at this temperature, thus illustrating the dimensional stability.

EXAMPLE IX

- 40 A sample of yarn obtained from a thio-amide* polymer composition was placed in the programmed furnace at 90° C. and heated to 300° C. at a rate of 11° C. per minute, and then heated at 5° C. per minute to 425° C. A sample of yarn was removed at this time and after the time intervals indicated thereafter. The following observations were made with reference to those samples.

Time at 425° C.:

- 50 (1) Zero—not quite flame proof
- (2) 12.5 minutes—dimensionally stable—still burns
- (3) 20.0 minutes—dimensionally stable and essentially flameproof
- (4) 25.0 minutes—dimensionally stable and flameproof

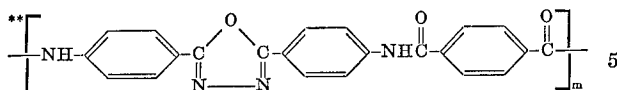


EXAMPLE X

- 65 A sample of yarn obtained from an oxazo-amide** polymer composition was placed in the programmed furnace at 90° C. and heated to 300° C. at a rate of 11° C. per minute, and then heated at a rate of 5° C. per minute to 425° C. Samples of yarn were removed after the time intervals indicated and tested for flameproofing, and dimensional stability. The following observations were made.

- 70 (a) after 67 minutes—samples burned readily
- (b) after 90 minutes—sample burns slowly—some dimensional stability apparent on short exposure to flame
- (c) after 225 minutes—sample completely flameproof, di-

mentally stable. The yarn was fairly strong but relatively brittle compared to previous examples.



Articles processed within the range of conditions specified in this invention can withstand moderate exposure to flames without deterioration, and are sufficiently flexible and dimensionally stable to permit use in practical applications requiring a high degree of thermal oxidative stability, such as for example, heat shields, high temperature and electrical insulation, protective clothing and curtains, composites and laminates, hot filtration media, supports for ablative materials and outer layers for materials that are exposed to flames. They are also excellent precursors for carbon and graphite fibers.

Fibers, filaments, films, fabrics and other shaped articles are conveniently treated by the process. Semicarbonized woven tapes or fabrics are particularly useful as flameproof outer coverings of various compositions. Fibers

which have been treated by the process, cannot be converted as easily into woven fabrics as the original fiber. Therefore, when woven tapes or fabrics are desired, it is sometimes preferred that these articles be prepared prior to processing.

The products of this invention are further characterized by their versatility with respect to flameproofing and dimensional stability. The process permits a semicarbonized fibrous product to be prepared having practically any desired level of heat resistance and tenacity. Completely flameproof fibers can be prepared with tenacities of around 0.5 g.p.d. A lesser degree of flameproofing may be sufficient for some applications and correspondingly better physical properties can be retained by virtue of the less severe treatments required.

Another surprising feature of the products of this invention is their insolubility in concentrated sulfuric acid, which is indicative of cross-linking; yet, they retain a high degree of flexibility. Although the relative elemental analysis is not substantially changed there is evidence of slightly lower oxygen and hydrogen contents in the semicarbonized product indicating that oxygen was serving in a hydrogen abstracting capacity and perhaps pointing to some crosslinking. No differences were detected in the multiple internal reflectance spectra of the semicarbonized and starting materials. This is an indication that no major structural changes have taken place.

The foregoing detailed description has been given for clearness of understanding only, and unnecessary limitations are not to be construed therefrom. The invention is not to be limited to the exact details shown and described since obvious modifications will occur to those skilled in the art, and any departure from the description herein

that conforms to the present invention is intended to be included within the scope of the claims.

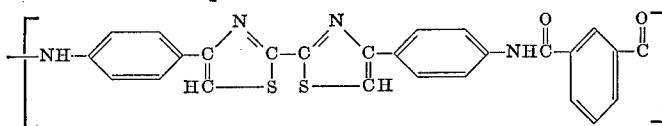
We claim:

1. A process for the semicarbonization of wholly aromatic polyamides to impart a carbon content thereto of between 70 percent and less than 90 percent by weight, said polyamides being in a form of high surface to volume ratio and having a threshold energy of activation for semicarbonization below the temperature at which structural identity and strength are lost, comprising subjecting the aromatic polyamide to a controlled heat sequence in air consisting of (1) raising the temperature of the polyamide incrementally from about 25° C. to a temperature in the range of from about 250° C. to 500° C. over a period of from about 45 minutes to 1 hour, (2) maintaining the polyamide at that temperature for a period of time ranging from 25 minutes to about 12 hours.

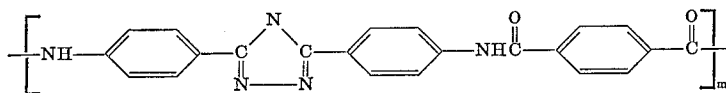
2. The process of claim 1 wherein the polyamide is poly-m-phenylenebis(m-benzamido)terephthalamide.

3. The process of claim 1 wherein the polyamide is poly-m-phenyleneisophthalamide.

4. The process of claim 1 wherein the polyamide is



5. The process of claim 1 wherein the polyamide is



6. The process of claim 1 wherein the polyamide is the polyterephthalamide of 4,4' - bis(4-aminobenzamido)diphenyl ether.

7. The process of claim 1 wherein the polyamide is poly-m-phenylenebis(benzamido)2,6-naphthalene dicarboxamide.

8. The polymeric product produced by the process of claim 1 characterized by insolubility in cold concentrated sulfuric acid and a capability for retaining structural integrity and dimensional stability when exposed to an open hydrocarbon flame.

9. The polymeric product of claim 8 in the form of a fiber.

10. The polymeric product of claim 8 in the form of a woven or non-woven fabric or web.

11. The polymeric product of claim 8 in the form of a cellular shaped article.

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