Abstract:

Disclosed is a moulded three-dimensional article obtained by moulding and acetylenically crosslinking at least one acetylenic polyamide or a composition comprising at least one acetylenic polyamide, which acetylenic polyamide by reaction is fitted with at least one acetylenic carbon-carbon triple bond derived from at least one acetylenic compound having at least one acetylenic carbon-carbon triple bond.
MOULDED ARTICLE OBTAINED FROM ACETYLENIC POLYAMIDE

The present invention refers to a three-dimensional moulded article obtained from an acetylenic polyamide or a composition comprising an acetylenic polyamide. Said acetylenic polyamide is obtained by incorporation of at least one acetylenic compound, having at least one carbon-carbon triple bond, into a polyamide.

Acetylenic above and hereafter refers to any chemical compound, including monomers, oligomers and polymers and/or any chemical group, which compound or group has at least one carbon-carbon triple bond.

Moulding is intended to mean moulding techniques in which the dimension along any given axes may be varied. This may be achieved by use of a mould with a cavity. Accordingly, such an embodiment encompasses injection moulding, extrusion, blow moulding and compression moulding. Crosslinking of the acetylenic polyamide may be performed either directly within the mould or separately and subsequent to the moulding.

Three-dimensional article is intended to mean an article, wherein the cross-section at any given axes, due to the moulding process used, may be varied. Accordingly, such an embodiment does not encompass articles, such as fibers, having a constant diameter.

Polyamides are polymers comprising recurring amide groups as integral parts of the main polymer chain. They can occur both naturally, examples being proteins such as wool and silk, and can be made artificially, examples being nylons, aramids and alkali, such as sodium, poly(aspartates). Nylon is a commonly used designation for the family of synthetic polymers known generically as polyamides. The amide link can for instance be produced by condensation reaction of an amino group and a carboxylic acid, anhydride or acid halide group. The amino groups and the carboxylic acid, anhydride or halide groups can be on the same monomer, such as an amino acid having at least one amino group and at least one carboxylic acid group, or the polymer can be built up from two or more different di, tri or polyfunctional monomers, such as one with two or more amino groups and one with two or more carboxylic acid, anhydride or acid halide groups.

Polyamides are typically condensation polymers formed by reacting equal parts of for instance a diamine and a dicarboxylic acid and a numerical suffix is often used to specify the number of carbons donated by the monomers, the amine first and the carboxylic acid second. The most common variant is polyamide 6,6 which refers to the fact that the diamine, hexamethylene diamine, and the diacid, adipic acid, each donate 6 carbons to the polymer chain. Accordingly, polyamide 5,10 is built up from pentamethylene diamine and sebacic acid, polyamide 6,12 is a
polyamide obtained from a C₆ diamine and a C₂ diacid, and similarly for polyamide 6,11, polyamide 10,12, and so on.

Further polyamides include polylactams which are not condensation polymers, but formed by a ring-opening polymerisation of a lactam, such as caprolactam yielding polycaprolactam also known as polyamide 6, aromatic polyamides, such as aramids, polymerised by the addition of aromatic di, tri or polyfunctional acids like terephthalic and isophthalic acid, copolymers of polyamide 6,6 and polyamide 6 and starbranched polyamides produced by condensation of for instance dicarboxylic acids with amines having three or more amino groups.

Polyamides are recognised as exhibiting good abrasion resistance, low friction coefficient, good resistance to heat and good impact resistance. Polyamides are in dry conditions good electrical insulators. Polyamides are typically hygroscopic and absorb water. This absorption will change some properties, such as insulation, tensile strength and stiffness. The impact resistance is increased by a higher content of water.

There are, despite the fact that polyamides have excellent physical and chemical properties and for a long time have been widely used for resins, films, fibres, moulded articles and so on, demands for improved and/or modified properties, such as increased operational temperatures increased flex modulus, increased stress-strain and retained properties during and after exposure to for instance harsh temperature, atmosphere, mechanical and radiation conditions.

Attempts to improve and/or alter the properties of polyamides have been made by crosslinking them, such as by UV or other radiation technology. However, these attempts have not been very successful. Furthermore, known method, which has relied on the incorporation of catalysts to assist the crosslinking, have the disadvantage that catalyst or catalyst by-products may leek from the article comprising the crosslinked polymer. Methods relying on the use of radiation to initiate crosslinking are only useful to affect the surface of an article comprising polymers to be crosslinked. Addition of additional components other than the polyamide may also negatively affect tolerance of the polymer in steps preceding the moulding of a polymeric article.

It has now quite unexpectedly been found that a moulded three-dimensional article, meeting said demands for improved and/or modified properties, can be obtained from acetylenic polyamides wherein at least carbon-carbon triple bond by reaction is incorporated into a polyamide, for instance as endcapping group, as pendant group along the molecular backbone and/or as group being part of the molecular backbone.
The present invention accordingly refers to a moulded three-dimensional article obtained by moulding, preferably in a mould cavity, at least one acetylenic polyamide, obtained by incorporation of at least one compound having at least one acetylenic carbon-carbon triple bond into a polyamide, or by moulding at least one composition comprising said at least one acetylenic polyamide. Articles as disclosed herein may be used as structural elements themselves. Such use is further elaborated below.

The purpose of the present invention is to modify the mechanical properties of polyamides and compositions comprising polyamides. Among these modifications of properties can be mentioned reduced melt viscosity, increased flex modulus and improved ability to counteract creep strain.

When used herein "acetylenic residue" or "residue comprising at least one acetylenic carbon-carbon triple bond" is intended to refer to a compound having at least one acetylenic carbon-carbon triple bond, which by reaction has been incorporated into a polyamide, for instance as endcapping group, as pendant group along the molecular backbone and/or as group being part of the molecular backbone.

Said acetylenic polyamide is preferably and in embodiments of the present invention either obtained by (A) subjecting at least one acetylenic compound to reaction with at least one polyamide, (B) by subjecting at least one acetylenic compound to reaction with at least one amine, aminoacid and/or lactam yielding a corresponding acetylenic amide monomer or oligomer, which acetylenic amide monomer or oligomer subsequently is used in production of an acetylenic polyamide or (C) by subjecting at least one acetylenic compound to co-polymerisation with at least one amine, aminoacid and/or lactam and at least one carboxylic acid or anhydride or a corresponding acid halide or alkyl ester, yielding a corresponding acetylenic oligoamide or polyamide. A yielded acetylenic oligoamide can be used in production of an acetylenic polyamide and a yielded acetylenic polyamide comprises preferably acetylic monomer residues having said at least one carbon-carbon triple bond in an amount corresponding to between 0.1 and 30 mol% of the total molar amount of monomer residues in said acetylenic polyamide.

The moulded three-dimensional article of the present invention is suitably obtained by moulding at least one said acetylenic polyamide or at least one composition comprising at least one said acetylenic polyamide. The acetylenic polyamide is, upon and/or subsequent said moulding, crosslinked by heat, provided externally or in situ generated, induced crosslinking reaction of its acetylenic group(s), optionally in presence of an effective amount of at least one compound promoting crosslinking reactions of acetylenic polymers, such as a sulphur or an...
organic sulphur derivative as disclosed in for instance US patent no. 6,344,523 and/or a radical initiator. It is understood that the acetylenic group of the acetylenic polyamide can be arranged as an endcapping, in-chain and/or pendent group. This will, of course in itself give different properties to the polymer after said crosslinking. The fact that the acetylenic residue is part of the polyamide and the relative high temperature needed to initiate crosslinking, means that standard process used in the manufacture of polymer articles comprising polyamides may be used also with acetylenic polyamides. These process includes steps such as granulation, compounding and injection moulding.

It is possible to further modify the mechanical properties of the moulded article of the present invention by using methods known in the art together with said acetylenic polyamide. The purpose of such modifications is typically to reinforce for strength, to fill for higher density, dimension stability and higher stiffness, adding of conductive materials for avoiding static charging and pigmentation for aesthetic properties.

It is also known in the art to add different types of fibres as reinforcements. Fibres suitable for use together with said acetylenic polyamide can be exemplified by glass fibres, carbon fibres, steel fibres, aramide fibres, natural organic fibres, such as cellulose fibres, flax fibres, cotton fibres and silk. However, most organic and inorganic fibres that are able to withstand the process temperatures may prove useful. It is also possible to use fullerenes for reinforcing as well as for changing other mechanical properties.

Fillers are typically used to increase dimension stability even though a few other mechanical properties, such as density, rigidity and acoustic properties may be altered by means of fillers. Fillers may be organic like cellulose or inorganic, such as minerals like for instance mica, lime and talcum.

It is furthermore possible to add stabilisers to said acetylenic polyamide, such as compounds stabilising obtained moulded article towards exposure to ultraviolet light, heat or other exposure that may cause for instance polymer chain breakdown. The possibility to add various kinds of fire retarding agents can in this context also mentioned.

It is yet furthermore possible to modify the properties of said moulded article by addition of plasticisers, lubricants or impact modifiers yielding for instance a polymer with elastic properties having improved thermal stability.

The electrical properties of the moulded article may also be modified within the scope of the invention. This may be achieved by addition of for instance an insulation modifier. The most common modifier is carbon black which is used in smaller quantities to achieve antistatic
properties. By adding higher amounts of carbon black, said moulded article obtained from said acetylenic polyamide and/or said composition, may exhibit from dissipating properties to conducting and shielding properties. There are besides carbon black also other known substances and compounds used for obtaining above or portions thereof. Metal fibres, carbon fibres and metal powder are only a few examples of such materials. Some of these materials also serve the purpose of reinforcing and filling agents.

Said acetylenic polyamide may also be expanded to change the density and thermal insulation property of obtained moulded article. This can be achieved by for instance addition of a blowing, expanding and/or foaming agent. This may of course be used in combination with other additives.

It is in some applications also advantageous to modify the surface properties of said moulded article. This includes for instance addition of anti-microbial agents for which the purpose is obvious. Another way is by adding so called tackifiers increasing friction if and when needed. Furthermore, the viscosity of the polymeric material during processing may be altered by means of rheology modifiers in order to obtain desired process parameters.

Acetylenic crosslinking/curing of said acetylenic polyamide is advantageously initiated by providing the mould, the inlet or the hotrunner with a choking valve or check valve arrangement creating heat in the polymer through friction caused during the injection phase. The valve arrangement may be a solid arrangement whereas the generated heat is guided through the velocity of injection. There are numerous ways to guide the injection velocity.

One way to guide the velocity is through PLC (Programmable Logic Controller) used for guiding the injection moulding parameters of most modern injection moulding machines. The operator will then have to perform a series of trials wherein the injection speed in small steps is increased until the threshold temperature in the valve arrangement is sufficient to initiate the curing process. The valve arrangement is advantageously made adjustable for the same purpose.

Another way is to guide the process actively by using a temperature sensor in the mould and/or in the valve arrangement. A pressure sensor advantageously arranged just before the valve arrangement, optionally with a second pressure sensor arranged after the valve arrangement, may serve the same purpose as it indicates the pressure drop and thereby the friction generated. The temperature and pressure sensor(s) may also be used in combination. Data generated from these sensors is then used as process data for guiding the injection moulding cycle. This data may then be used for guiding the injection sequence through direct guiding or so-called
statistical process guiding. Statistical process guiding is especially advantageous where there is
a risk for measurement lag, data delay or process guiding resonance in the process.
It is also possible to design in such a way that choking portions in the mould itself will constitute a part of the article produced. It will in this way be possible:
  a) to manufacture articles that due to its size or through very quick curing of used polymers otherwise would be impossible to manufacture, and/or,
  b) to manufacture articles wherein only certain portions are cured, while other portions have the properties of an uncured polymer.

It is furthermore possible to actively guide the orifice size of the check valve thus allowing the temperature profile to be guided through other means than only the injection speed. This can for example be achieved through means of an hydraulic actuator constantly adjusting the size of the opening through the check valve. This guiding can be performed through PLC data only or by the aid of measuring data in the mould and/or around the valve as described above.

The check valve may also be provided with guided heating and/or cooling, either as a replacement for mechanically adjusting of the orifice size, or as a complement thereto. This can also be guided through PLC data only or by the aid of measuring data in the mould and/or around the valve as described above.

The mould is advantageously provided with one or more temperature sensors for the purpose of detecting the exothermic heat caused by the curing process. It is suitable to arrange several such sensors along the flow path of the polymer in order to detect variations in the curing in different portions of the article produced. These measurements are suitably used for statistical process guiding.

Similar principles as described above may be used in extrusion moulding. It will, however, be rather easy to achieve a favourable temperature profile for the curing where the polymer material is first plasticised, then heated further in the extrusion mould to initiate the curing while the later portions of the extrusion mould will cool the article enough to keep its shape. The continuous nature of the process is well suited for the curing of the acetylenic polyamide herein disclosed. Further heating is advantageously achieved by heating a predetermined portion of the extrusion mould by means of an external heat source. This will allow the operator to guide the curing process not having to rely completely on the extrusion velocity for heat generation.

The herein disclosed moulded article is well suited for use in a compression moulding process. A predetermined amount of polymeric material can here be preheated to a temperature somewhat under the curing temperature and placed in an open mould. The mould is then
closed so that the polymeric material is distributed in the mould as is the normal procedure in compression moulding. The preheating, the mould temperature, the viscosity of the polymeric material and the compression pressure is adapted so that the friction and compression pressure will generate the heat needed to initiate the curing. It is also in a compression moulding process advantageous to provide the mould with one or more temperature and/or pressure sensors for the purpose of detecting the exothermic reaction during the curing.

The disclosed moulded article is also well suited for different kinds of blow moulding processes were a melted preformed material is extruded into an open cavity which then is closed and pressurized so that a partly hollow three dimensional moulded article produced.

The temperature initiating curing is depending on the structure of the acetylenic portion of the acetylenic polyamide and will have to be adapted to avoid material break down of the polymer chain on curing. There are several ways to modify the acetylenic portion as disclosed in the present application. There is also the possibility to modify the curing temperatures by utilising a catalyst or initiator. Catalysts have proven to radically lower the curing initiation temperature. It is also possible to add coupling agents.

It is, according to one alternative embodiment of the invention possible to perform at least a portion of the curing after the moulding process. This can for example be performed through electron beam (EB) curing or ultraviolet (UV) curing. This will also call for the need of for instance one or more photoinitiators. In most applications only a surface curing can be achieved through means of UV curing since the thermoplastic polymer is not transparent, however EB curing will be possible to utilise even for opaque polymers. Surface curing can also be performed through corona treatment or flash heating. It will through this process be possible to cure the surface of a produced article without softening the polymeric material.

According to one embodiment, the curing temperature, i.e. the temperature above which crosslinking takes place is higher than the melting temperature, such as at least 20, 40, 80 or 100°C higher, than the melting temperature of the acetylenic polyamide. In such an embodiment the acetylenic polyamide may be moulded into a three dimensional article without initiating crosslinking if desired or by increasing the temperature in the mold or at the end of the process achieve a crosslinked three dimensional article. Furthermore, and importantly the acetylenic polyamide may thus be processed without initiating crosslinking. Accordingly, additives to a composition comprising an acetylenic polyamide, such as fillers, stabiliser, plasticiser, lubricant, impact modifier, photoinitiator and blowing, expanding and/or foaming agents, may be added and mixed with the acetylenic polyamide without initiating crosslinking.
It is also possible to continue an initiated curing at a lower temperature. The article produced is here after the moulding procedure placed in an oven for a period of time ranging from half an hour to a couple of days. This process is known as baking. In order to keep important portions of the article, such as the flange portion of an oil pan, within desired tolerances the article may be arranged on a jig during the curing process.

The herein disclosed three-dimensional moulded article used within, but not limited to, civilian and military transportation vehicles, such as cars, trucks, busses, motorcycles, trains, ships and aircrafts as well as recreational vehicles wherein for instance demands for weight reduction is an increasing demand.

Further suitable application areas include automotive, aeronautic and aerospace components, such as exterior body panels and glazing, including back lights, door panels, fenders, panoramic roofs, roof modules, tailgates, heat shields, armours and spall linings. Further suitable articles include exterior components, such as vent grilles, door handles, front grilles, mirror systems, roof racks, running boards, spoilers, tank flaps, wheel housings and wheel covers as well as traditional after market products. It is also possible to produce larger components for trucks, busses, ships and aircrafts. Yet further suitable articles include lighting, such as fog lamp lenses, reflectors and housings; headlamp bezels, housings, lenses and reflectors; lamp support brackets; projector lamp reflectors and holders; rear combination lamp housings, reflectors and lenses. These articles can be base coated, primed for painting, direct metallised and/or moulded in colour. The three-dimensional article of the present invention may also include other structural as well as interior components, such as composite headliners, energy absorption systems, front end modules, instrument panels, interior trimmings, load floors, pedestrian energy absorption systems and storage bins, as well as parts suitable for motorcycles, such as no-paint parts, tanks, fairing, chassis, frames, luggage containers and racks, as well as motorcycle rider safety items, such as helmets and all sorts of shields. Further application areas for moulded articles produced from acetylenic polyamides include power train parts, such as air intake, automotive gears, wire coatings, brackets, sealings, electronic and electronic housings, fuel system components, pulleys, sensors, throttles bodies, transmissions and transmission parts, and valve rocker covers as well as other components in vehicle engine bays wherein heat may render prior art polymers insufficient.

Further suitable moulded articles include, but are not limited to, moulded articles used in home entertainment, such as television apparatus and equipment, projectors and audio devices, as well as mobile entertainment and information carriers and communication devices, such as antennas, satellite dishes, as well as articles and devices for recreation, entertainment and sport activities wherein for instance the weight to strength ratio is important, such as light weight components in extreme sport equipment including body protection, parts to mountain bikes,
heat shields and the like. Yet further suitable articles include for instance fishing rods and golf clubs.

A further industry having demands on higher mechanical strength, sometimes under elevated temperatures, is the packaging industry. The use of moulded articles according to the present invention will solve a number of problems linked to medium to long term storage under for instance elevated temperatures. Furthermore, creep strain in polymers, which today is a problem calling for over-dimensioning of carrying structures made of polymeric materials, can be eliminated or reduced by use of a moulded article according to the present invention.

It is also advantageous to utilise a moulded article as herein disclosed in household, building and construction industry, including, but not limited to beams, girders, rails, panels, window frames and sub assemblies, roofing, flooring, doors and door frames, handles, knobs, cabinets, housings, kitchen appliances and central heating and energy recovery systems as well as solar energy collectors and other parts of solar and wind energy and heating systems and equipment. Further application areas can be found among electrical components, equipment and installations, such as circuit breakers, films, flexible and rigid wire coatings, housings and discrete components.

The herein disclosed three-dimensional article is also suitably an article used in health care, including man and animal, and laboratory equipment, such as cardiovascular and blood care equipment, oxygenators, filters, pumps, masks, sleep therapy equipment, drug delivery devices, inhales, syringes, injection devices, stopcocks and valves as well as orthopedic equipment, external bone fixation, joint trials, mechanical instruments, surgical instruments, electrosurgical instruments, endomechanical instruments and access devices as well as sub components and spare parts to the above. Said article is furthermore a three-dimensional moulded article used for supporting, diagnostic and monitoring equipment, such as hand instruments, equipment for imaging, ocular devices, dental devices, laboratory ware and vials as well as sterilisation trays.

The acetylenic polyamide having at least carbon-carbon triple bond obtained by incorporation of at least one acetylenic compound having at least one acetylenic carbon-carbon triple bond can suitably be exemplified by linear or branched aliphatic, cycloaliphatic and/or aromatic acetylenic polyamides comprising monomer units derived from at least one said acetylenic compound and in addition thereto at least one linear or branched aliphatic, cycloaliphatic or aromatic di, tri or polyfunctional amine and at least one linear or branched aliphatic, cycloaliphatic or aromatic di, tri or polyfunctional carboxylic acid or anhydride or a corresponding acid halide or alkyl ester and/or at least one aliphatic, cycloaliphatic or aromatic aminoacid and/or at least one lactam. Said amine, aminoacid and/or lactam has preferably
Such acetylenic polyamide comprises in its most preferred embodiments amine functional monomer units derived from the group consisting of hexamethylene diamine, pentamethylene diamine, 2,2,4-trimethyl-hexamethylene diamine, 2,4,4-trimethyl-hexamethylene diamine, 1,4-diaminobutane, 11-aminoundecanoic acid, 12-aminodecanoic acid, aminocaproic acid, 1,2-diaminobenzene, 1,3-diaminobenzene, 1,4-diaminobenzene and carboxyfunctional monomer units derived from the group consisting of oxalic acid, malic acid, adipic acid, sebacic acid, isophthalic acid, terephthalic acid and 2,5-furandicarboxylic acid. Further preferred monomer units include those derived from for instance caprolactam and laurolactam.

Said acetylenic compound can likewise suitably be exemplified by acetylenic aromatic compounds of Formula I through VIE.

**Formula I**

![Formula I](image)

**Formula II**

![Formula II](image)

**Formula III**

![Formula III](image)

**Formula IV**

![Formula IV](image)
wherein the position in the aromatic ring of the acetylenic (carbon-carbon triple bond) is variable and wherein each substituent R individually is hydrogen or a hydroxy, halo or amino group or a linear or branched alkyl, alkenyl, alkynyl, aminoalkyl, aminoalkenyl, aminoalkynyl, haloalkyl, haloalkenyl, haloalkynyl, hydroxyalkyl, hydroxyalkenyl, hydroxyalkynyl, hydroxyacyl or aminoacyl group or an aryl, hydroxyaryl or aminoaryl group, each substituent R\(^1\) individually is hydrogen or a hydroxy or halo group or a linear or branched alkyl, alkenyl, hydroxyalkyl, hydroxyalkenyl, haloalkyl or haloalkenyl group, each R\(^2\) individually is a linear or branched alkyl, alkenyl, alkynyl or acyl group and each R\(^3\) individually is a linear or branched alkyl, alkenyl or alkynyl group or an aryl group.

Further suitable acetylenic compounds are found in the group consisting of acetylenic linear or branched aliphatic, cycloaliphatic or aromatic carboxylic acids, anhydrides and corresponding acid halides and alkyl esters, such as alkynyl, alkylalkynyl and arylalkynyl o-phthalic acids and anhydrides, alkynyl and arylalkynyl isophthalic acids, alkynyl and arylalkynyl terephthalic acids, alkynyl and arylalkynyl benzoic acids, alkynyl and arylalkynyl adipic acids, alkynyl and arylalkynyl azelaic acids, alkynyl and arylalkynyl sebacic acids, alkynyl and arylalkynyl furandicarboxylic acids and corresponding acid halides and alkyl esters.
Said aryl is above preferably phenyl or naphthyl, said alkyl likewise preferably linear or branched, aliphatic or cycloaliphatic Ci-Cs alkyl, such as methyl, ethyl, propyl or butyl, said alkenyl likewise preferably aliphatic or cycloaliphatic, linear or branched C₂-C₈ alkenyl, such as ethenyl, propenyl or butenyl, and said alkynyl likewise preferably aliphatic or cycloaliphatic, linear or branched C₂-C₈ alkynyl, such as ethynyl, propynyl or butynyl.

The most suitable acetylenic compounds can be exemplified by ethynyl o-phthalic anhydride, methylethynyl o-phthalic anhydride, phenylethynyl o-phthalic anhydride, naphthylethynyl o-phthalic anhydride, ethynyl isophthalic acid, methylethynyl isophthalic acid, phenylethynyl isophthalic acid, naphthylethynyl isophthalic acid, ethynyl terephthalic acid, methylethynyl terephthalic acid, phenylethynyl terephthalic acid, naphthylethynyl terephthalic acid, ethynyl benzoic acid, methylethynyl benzoic acid, naphthylethynyl benzoic acid, ethynyl adipic acid, methylethynyl adipic acid, phenylethynyl adipic acid, naphthyl-ethynyl adipic, ethynyl azaleic acid, methylethynyl azaleic acid, phenylethynyl azaleic acid, naphthylethynyl azaleic, ethynyl sebacic acid, methylethynyl sebacic acid, phenylethynyl sebacic acid, naphthylethynyl sebac, ethynyl 2,5-furandicarboxylic acid, methylethynyl 2,5-furandicarboxylic acid, phenylethynyl 2,5-furandicarboxylic acid, naphthylethynyl 2,5-furandicarboxylic acid and/or a corresponding acid halide or alkyl ester.

Further and especially suitable embodiments the acetylenic compound may be selected from the group consisting of compounds according to Formula IX and X

![Formula IX](image)

![Formula X](image)

wherein R¹ is as defined above; one or two of R⁴ to R⁸ is C(O)R¹⁴, the others being, independent of each other, hydrogen, halo, C⁰⁻³ alkandiylNR¹⁵⁴ and R¹⁶, independent of each other, are hydrogen or C₁⁻⁵ alkyl, such as NH₂, NMe₂ and Ci alkandiylNH₂, C⁰⁻₃ alkandiylOCo⁻₃ alkyl, such as hydroxy, methylenehydroxy and methoxy, C(0)Co⁻₃ alkyl, such as acetyl, CI⁻₄ haloalkyl, such as C₁⁻₄ fluoroalkyl, such as trifluoromethyl, OC(0)Co⁻₃ alkyl, such as acetoxy; R⁹ to R¹³ are, independent of each other,
hydrogen, C(O)R$_{\text{14}}$, halo, Co-3 alkandiylnR$_{\text{15}}$R$_{\text{16}}$, wherein, R$_{\text{15}}$ and R$_{\text{16}}$, independent of each other, are hydrogen or C$_{\text{1}}$C$_{\text{5}}$ alkyl, such as NH$_{\text{2}}$, NMe$_{\text{2}}$ and C$_{\text{i}}$ alkandiylnH$_{\text{2}}$,Co-3 alkandiyloCo-3 alkyl, such as hydroxy, methylenehydroxy and methoxy, C(O)Co-3 alkyl, such as acetyl, C$_{\text{1}}$C$_{\text{4}}$ haloalkyl, such as C$_{\text{i}}$-4 fluoroalkyl, such as trifluoromethyl, OC(O)Co-3 alkyl, such as acetoxy; R$_{\text{14}}$ is, independent of each other if more than one R$_{\text{14}}$ is present, OH, OC$_{\text{i}}$C$_{\text{8}}$ alkyl, such as OMe, OC(O)Ci$_{\text{s}}$ alkyl, such as OC(O)Me, NCO-3 alkylC(O)Ci$_{\text{s}}$ alkyl, such as NHC(O)Me, NHC$_{\text{2}-12}$ alkandiylnH$_{\text{2}}$, such as NHC$_{\text{6}}$ alkandiylnH$_{\text{2}}$, or halogen, such as chlorine; further, if two C(O)R$_{\text{14}}$ are present on adjacent atoms, i.e. ortho or 1,2 with respect to each other, in any of the benzene rings in Formula IX and X, a single R$_{\text{14}}$ may be connected to both carbonyls, and accordingly being part of a 5-membered ring; R$_{\text{14}}$ may then be "O" or NR$_{\text{15}}$, wherein R$_{\text{15}}$ is hydrogen, C$_{\text{2}-8}$ alkandiylnH$_{\text{2}}$ or phenylH$_{\text{2}}$.

Preferably, one or two of R$_{\text{4}}$ to R$_{\text{8}}$ is C(O)R$_{\text{14}}$ and the others are hydrogen. Furthermore, it is preferred if R$_{\text{1}}$ is hydrogen or linear or branched C$_{\text{1}}$C$_{\text{4}}$ alkyl. It is also preferred that R$_{\text{5}}$ is C(O)R$_{\text{14}}$. If R$_{\text{5}}$ and R$_{\text{6}}$ are C(O)R$_{\text{14}}$, then it is preferred that R$_{\text{4}}$, R$_{\text{7}}$ and R$_{\text{8}}$ are hydrogen. Similarly, if R$_{\text{4}}$ and R$_{\text{5}}$ are C(O)R$_{\text{14}}$, then it is preferred that preferred that R$_{\text{6}}$ to R$_{\text{8}}$ are hydrogen.

According to one embodiment, Formula X is symmetrical with respect to the triple bond, the two benzene rings thus having the same substitution pattern, such as R$_{\text{5}}$, R$_{\text{6}}$, R$_{\text{10}}$ and R$_{\text{11}}$ being C(O)R$_{\text{14}}$. Such symmetrical compounds may be useful to connect different polyamides to each other.

According to one embodiment R$_{\text{5}}$ and R$_{\text{6}}$ are both C(O)R$_{\text{14}}$ and a single R$_{\text{14}}$, being "O" or NR$_{\text{15}}$, is connected to both carbonyls. Formula IX and X thus represents a phthalic anhydride residue or phthalimide residue in such an embodiment. Furthermore, it is preferred if R$_{\text{4}}$, R$_{\text{7}}$ and R$_{\text{8}}$ are hydrogen in such an embodiment.

In one preferred embodiment R$_{\text{5}}$ and R$_{\text{6}}$ are both C(O)R$_{\text{14}}$, R$_{\text{4}}$ or R$_{\text{7}}$ and R$_{\text{8}}$ are hydrogen and both R$_{\text{14}}$ are NHC$_{\text{2}-8}$ alkandiylnH$_{\text{2}}$.

As used in Formula IX and X, haloalkyl and haloalkandiyl, used alone or as a suffix or prefix, refers to groups in which one, two or three of the hydrogen(s) attached to any of the carbons of the corresponding alkyl and alkyne are replaced by halogen. Examples of haloalkyl include, but are not limited to, trifluoromethyl, difluoromethyl, fluoromethyl, 2,2,2-trifluoroethyl, 2-fluoroethyl and 3-fluoropropyl. Examples of fluoroalkylene include, but are not limited to, difluoromethylene, fluoromethylene, 2,2-difluorobutylene and 2,2,3-trifluorobutylene.
As used in Formula IX and X, alkyl used alone or as a suffix or prefix, is intended to include both branched and straight chain saturated aliphatic hydrocarbon groups having from 1 to 12 carbon atoms or if a specified number of carbon atoms is provided then that specific number is intended. For example C₆₋₅ alkyl denotes alkyl having 1, 2, 3, 4, 5 or 6 carbon atoms. When the specific number denoting the alkyl-group is the integer 0 (zero), a hydrogen atom is intended as the substituent at the position of the alkyl group. For example, N(Co alkyl)₂ is equivalent to NH₂ (amino).

As used in Formula IX and X, alkandiyl or alkylene used alone or as a suffix or prefix, is intended to include straight chain saturated aliphatic hydrocarbon groups having from 1 to 12 carbon atoms or if a specified number of carbon atoms is provided then that specific number is intended. For example C₁₋₆ alkandiyl and C₁₋₆ alkylene denotes alkandiyl or alkylene having 1, 2, 3, 4, 5 or 6 carbon atoms. When the specific number denoting the alkandiyl or alkylene group is the integer 0 (zero), a bond is intended to link the groups onto which the alkandiyl or alkylene group is substituted. For example, NH(Co alkylene)NH₂ is equivalent to NHNH₂ (hydrazino). Examples of alkyl include, but are not limited to, methyl, ethyl, w-propyl, /so-propyl, n-butyl, iso-butyl, sec-butyl, tert.-butyl, penty1 and hexyl. Examples of alkandiyl or alkylenyl include, but are not limited to, methylene, ethylene, propylene and butylene.

Preferred embodiments the compound having at least one acetylenic carbon-carbon triple bond is incorporated into the polyamide by formation of an amide bond. Accordingly it is preferred if the compound having at least one acetylenic carbon-carbon triple bond also has at least one carboxy group, alkoxy carbonyl group, haloformyl group and/or amine group. The compound having at least one acetylenic carbon-carbon triple may also comprise a phthalic anhydride residue or phthalimide residue. Preferably, the compound having at least one acetylenic carbon-carbon triple bond comprise a phthalic anhydride residue, such as a 2-benzofuran-1,3-dione residue.

A composition comprising said at least one acetylenic polyamide as disclosed above can in various embodiments further comprise at least one additional polymer, such as at least one additional polyamide and/or at least one filler, reinforcement, pigment, plasticiser and/or any other additive disclosed above and/or known in the art. Said acetylenic polyamide is in a said composition preferably present in an amount of between 0.1 and 99.9, such as between 1 and 40 or between 1 and 25, % by weight of said composition.

Without further elaboration, it is believed that one skilled in the art can, using the preceding description, utilise the present invention to its fullest extent. The following preferred specific embodiments are, therefore, to be construed as merely illustrative and not limitative of the
remainder of the disclosure in any way whatsoever. In the following, Examples 1-3 illustrate preparation of acetylenically crosslinkable polyamides and Example 4 refers to manufacturing and testing of three-dimensional moulded articles according to embodiments of the present invention. Test result is given in Table 1 and Graph 1.

Example 1

Step 1: 30 parts by weight of phenylethynyl phthalic anhydride was charged in a reaction vessel and dissolved at room temperature and under nitrogen purge in 50 parts by weight of tetrahydrofuran and 150 parts by weight of chloroform. 14.8 parts by weight of hexamethylene diamine was subsequently during 5 minutes added to the mixture. The temperature increased by 15-20°C due to the exothermic reaction. The temperature was further increased and kept at 55°C for two hours during which a solid was formed. The reaction was stopped and the solvents were removed. Obtained product was for 24 hours dried in an oven at 60°C to yield a yellowish solid acetylenic amide monomer. GC analysis confirmed that both the organic solvent and the product contained less than 0.2% by weight of unreacted phenylethynyl phthalic anhydride and thus a conversion of almost 100%.

Step 2: 86.1 parts by weight of hexamethylene diamine, 26.5 parts by weight of triethylamine and 3.9 parts by weight of the acetylenic amide monomer obtained in Step 1 were charged in a reaction vessel, equipped with nitrogen purge, and dissolved in 173 parts by weight of chloroform. The mixture was mechanically stirred at room temperature and 89.1 parts by weight of adipoyl chloride dissolved in 35 parts by weight of chloroform was added during 5 minutes. The reaction mixture was left over night at slow stirring. Chloroform and excess of triethylamine were now removed by evaporation and the mixture was poured into 1000 parts by weight of water and was allowed to agitate for 2 hours. The solid was filtered off and washed with 50 parts by weight of HCl (IM) followed by washing with 3 x 100 parts by weight of water. Obtained solid product was dried at 55°C for 6 hours to give a yellowish acetylenic polyamide 6,6 having a melting point of 250°C as determined by DSC analysis and an acetylenic content corresponding to 12% by weight of bonded phenylethynyl phthalic anhydride.

Example 2

86.1 parts by weight of hexamethylene diamine, 26.5 parts by weight of triethyl amine and 6.45 parts by weight of the acetylenic amide monomer obtained in Step 1 of Example 1 were charged in a reaction vessel, equipped with nitrogen purge, and dissolved in 173 parts by weight of chloroform. The mixture was mechanically stirred at room temperature and 94 parts by weight of adipoyl chloride dissolved in 35 parts by weight of chloroform was added during
5 minutes. The reaction mixture was left over night at slow stirring. Chloroform and excess of triethyl amine were now removed by evaporation and the mixture was poured into 900 parts by weight of water and was allowed to agitate for 2 hours. The solid product was filtered off and washed with 50 parts by weight of HCl (IM) followed by washing with 3 x 75 parts by weight of water. Obtained solid product was dried at 55°C over night yielding a yellowish acetylenic polyamide 6,6 having a melting point of 251°C as determined by DSC analysis and an acetylenic content corresponding to 17% by weight of bonded phenylethynyl phthalic anhydride.

Example 3

Step 1: 167.1 parts by weight of dimethyl adipate and 123.6 parts by weight of hexamethylene diamine were charged in a reaction vessel and under nitrogen purge heated to 40°C. 15 parts by weight of sodium methoxide was now added as reaction catalyst and the mixture was heated to 70°C and kept for 7 hours until a solid product phase precipitated. Obtained solid oligoamide having an average molecular weight of approx. 260 g/mol was washed with 2 x 200 parts by weight of water and dried in an oven at 50°C over night.

Step 2: 60.2 parts by weight of the oligoamide obtained in Step 1 above and 12 parts by weight of the acetylenic amide monomer obtained in Step 1 of Example 1 were mixed and heated over nitrogen to a melt at 230°C. The temperature was during 2 hours increased to 270°C and the mixture was kept at 270°C for a further 3 hours. The reaction mixture was now allowed to cool to yield a brownish solid product. Obtained acetylenic polyamide 6,6 had a melting point of 236°C as determined by DSC analysis and an acetylenic content corresponding to 11% by weight of bonded phenylethynyl phthalic anhydride.

Example 4

Two acetylic polyamides were, in accordance with the procedure of Example 1, produced from a mixture of polyamide 6 and polyamide 6,6 and phenylethynyl phthalic anhydride (PEPA) in an amount of 2.5 and 5 % by weight. Unmodified polyamide 6/6,6 mixture was used as reference.

The two acetylenic and the unmodified polyamides were injection moulded in an injection moulding machine (Engel, Austria) equipped with a tool for test plate manufacturing containing a cavity with the dimensions 100 x 100 x 2 mm. The barrel temperature was set to 180-320°C (from the inlet to the end zone) and the nozzle temperature was set to 340°C. Injection time was as set to 0.3 seconds, but in reality the time was slightly longer (0.5-0.8
seconds) due to operational limitations in the equipment. The injection moulding process was run until steady-state conditions were achieved and test plates were subsequently collected.

DSC analysis of the sample materials showed that the yield of the crosslinking reaction was about 50% for the sample yielded from reaction between the polyamide 6/6,6 mixture and 2.5% by weight of PEPA and about 40% for the sample yielded from reaction between the polyamide 6/6,6 mixture and 5% by weight of PEPA. Free (unreacted) PEPA was not possible to extract from the sample plates. Material testing was performed on all three samples. Material testing consisted of mechanical tests of 7 plates of each material. The test method used was flexural testing in bending mode (3-point bending tests) according to ISO 178:2001 and ASTM D790 standard procedure with a deformation rate of 0.1 mm/s. The result from said testing recorded an increased flexural modulus for samples made of acetylenic polyamides compared to the reference sample. The test result is below in Table 1 and Graph 1 (stress-strain comparison).

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<tr>
<th>PEPA Amount % by weight</th>
<th>Flex modulus Gpa</th>
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<tr>
<td>0</td>
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<tr>
<td>2.5</td>
<td>1.81</td>
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<td>5</td>
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Graph 1
CLAIMS

1. A moulded three-dimensional article
characterised in, that said article is obtained by moulding and acetylenically
crosslinking at least one acetylenic polyamide or a composition comprising at least one
acetylenic polyamide, which acetylenic polyamide comprises at least one acetylenic
residue having at least one acetylenic carbon-carbon triple bond.

2. A moulded three-dimensional article according to Claim 1
characterised in, that said at least one acetylenic residue having at least one
carbon-carbon triple bond is present in an amount corresponding to between 0.1 and 30
mol% of total molar amount of monomeric residues in said acetylenic polyamide.

3. A moulded three-dimensional article according to Claim 1 or 2
characterised in, that said article is moulded by injection moulding, blow
moulding, extrusion moulding or compression moulding.

4. A moulded three-dimensional article according to any of the Claims 1-3
characterised in, that said moulding is performed in a mould cavity.

5. A moulded three-dimensional article according to any of the Claims 1-4
characterised in, that said composition in addition to said at least one
acetylenic polyamide comprises at least one fibre as reinforcement.

6. A moulded three-dimensional article according to Claim 5
characterised in, that said fibre is selected from the group consisting of glass
fibres, carbon fibres, steel fibres, aramide fibres and natural organic fibres, such as
cellulose fibres, flax fibres, cotton fibres and silk.

7. A moulded three-dimensional article according to any of the Claims 1-6
characterised in, that said composition additionally comprises at least one
filler, such as a cellulose or an inorganic filler.

8. A moulded three-dimensional article according to Claim 7
characterised in, that said filler is selected from the group consisting of mica,
lime, talcum, carbon black and a metal powder.

9. A moulded three-dimensional article according to any of the Claims 1-8
characterised in, that said composition additionally comprises at least one
plasticiser, lubricant, impact modifier, fire retardant and/or photoinitiator
10. A moulded three-dimensional article according to any of the Claims 1-9 characterized in, that said composition additionally comprises at least one UV stabiliser.

11. A moulded three-dimensional article according to any of the Claims 1-10 characterized in, that said composition additionally comprises at least one blowing, expanding and/or foaming agent.

12. A moulded three-dimensional article according to any of the Claims 1-11 characterized in, that said composition additionally comprises at least one anti-microbial agent.

13. A moulded three-dimensional article according to any of the Claims 1-12 characterized in, that said composition comprises between 0.1 and 99.9%, such as between 1% and 40% or preferably between 1% and 25%, by weight of said acetylenic polyamide.

14. A moulded three-dimensional article according to any of the Claims 1-13 characterized in, that said acetylenic crosslinking is obtained by heat induced crosslinking of said carbon-carbon triple bond, optionally in presence of an effective amount of at least one compound promoting crosslinking reactions of acetylenic carbon-carbon triple bonds.

15. A moulded three-dimensional article according to Claim 14 characterized in, that said acetylenic crosslinking is performed during or subsequent said moulding.

16. A moulded three-dimensional article according to Claim 14 or 15 characterized in, that said heat is externally provided or in situ generated.

17. A moulded three-dimensional article according to any of the Claims 1-16 characterized in, that acetylenic crosslinking of said acetylenic polyamide is performed by in situ generated friction heat during injection.

18. A moulded three-dimensional article according to any of the Claims 1-14 characterized in, that acetylenic crosslinking of said acetylenic polyamide is performed by baking.
INTERNATIONAL SEARCH REPORT

International application No.
PCT/SE2009/000419

A. CLASSIFICATION OF SUBJECT MATTER

IPC: see extra sheet
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC: C08G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE, DK, FI, NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
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<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
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Further documents are listed in the continuation of Box C. See patent family annex.

Date of the actual completion of the international search: 14 December 2009

Date of mailing of the international search report: 8-12-2009

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International patent classification (IPC)
C08G 69/48  (2006.01)
C08F 299/02  (2006.01)
C08G 69/02  (2006.01)
C08G 69/26  (2006.01)

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Cited literature, if any, will be enclosed in paper form.
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