

Description

The invention relates to polyamide moulded articles consisting of a plurality of layers. Such moulded articles are known from JP-A-56008239, which describes a production process in which a preform of a thermoplastic resin is introduced into a mould, which is subsequently after-filled with the resin. Either the preform or the after-filled resin contains fibrous reinforcement. The preferred thermoplastic resins mentioned are polyamides such as nylon 6; nylon 6,6, nylon 6,10, nylon 6,12, nylon 11 and nylon 12, polyesters, polyolefins and polystyrenes. Reinforcing fibrous materials are glass fibre, carbon fibre, asbestos fibre, metal fibre, aromatic polyamide fibre, etc. The products obtained have a good rigidity and a smooth surface.

Technological progress implies that users will make higher and higher, combined in many cases with more and more, demands on products they want to use.

Thus the use, for instance, in the automotive industry requires, in addition to rigidity and smooth surface, a high impact resistance, a continuously improved temperature resistance and in many cases a good paintability or metallizability. In electronics dimensional stability at fluctuating temperatures and a sometimes very good adhesion of metal layers plays a special part, in addition to rigidity and smooth surface, and in the lighting industry where, owing to miniaturization, smaller and smaller and increasingly complex forms of reflectors are required, which must consequently also have an improved temperature resistance and dimensional stability, the processability plays a major part, in addition to the metallizability of the surface.

The polyamide multi-layer moulded articles with fibrous reinforcement as described in JP-A-56008239 cannot properly satisfy these increased and combined demands.

For that reason the object of the invention is to develop a multi-layer moulded article, which can be obtained in a simple conventional manner, which meets the requirements in respect of rigidity and smoothness of surface as known from the state of the art and which also has an improved dimensional stability while retaining impact resistance, a higher temperature resistance and an improved adhesion for metal layers or paints.

After intensive research it has now been found that by applying the polyamide nylon 4,6 as thermoplastic resin and a non-fibrous filler instead of fibrous reinforcing materials a multi-layer moulded article is obtained that complies with these increased and combined demands.

The multi-layer polyamide moulded article according to the invention comprises a filler-reinforced polyamide layer covered on at least one side with a non-reinforced polyamide layer, characterized in that

- a. the polyamide is substantially composed of tetramethylenedipamide units
- b. the filler is predominantly non-fibrous.

The filler may in principle have all forms, such as the form of a powder, globules, non-rounded particles, small plates and even small bars, the length : width ratio being not higher than 10 : 1, preferably smaller than 3 : 1. Filler in the form of fibres must be avoided, because otherwise, owing to anisotropic effects, generally no homogeneous dimensional stability is obtained. A minor amount of fibrous material (i.e. less than 50% (wt) preferably less than 30 % (wt) of the total amount of fillers) is permissible indeed provided, owing to the presence of the other fillers, the anisotropic effect by the presence of the fibrous material in, for instance, the injection moulding of moulded parts is sufficiently disturbed due to the presence of an excess of non-fibrous fillers. The filler preferably consists of powdery, plate-shaped or spherical material. Highly suitable fillers are talcum, mica and lime.

The concentration of the filler in the filler-containing layer may vary within very wide limits, for instance between 10 and 80% (wt) calculated on the total weight of the layer. The content is preferably between 25 and 60% (wt). Depending on the filler used, the best result is achieved with a content between 35 and 55% (wt).

The polyamide according to the invention may be a homopolyamide, a copolyamide or a polyamide mixture and is substantially composed of tetramethylene-adipamide units, for instance at least 75% of the number of units, preferably the number of tetramethylenedipamide units amounts to more than 85%; even more advantageous is a content of at least 90% tetramethylenedipamide units. The best results are achieved with homopolymer. There is generally no restriction as to the copolymerization component or to the blend component, and for instance all known amide-forming substances can be used. Examples of copolymerization components are amino acids, lactams, diamines and dicarboxylic acids. Examples of blend components are the polyamides formed from the above-mentioned copolymerization components. However, other monomers, too, and polymers formed from these, for instance ester-forming monomers, respectively polyester can be applied.

The polyamide substantially composed of tetramethylenedipamide units can be obtained in various

ways known per se. Preferred preparation processes are described in, inter alia, US-A-4408036 and US-A-4460762. The degree of polymerization of the polyamide is not limited and in the reinforced layer it is usually such that the relative viscosity measured on a solution of 1 grām in 100 ml 96%-(wt) sulphuric acid is at least 2.0, preferably at least 2.5. The degree of polymerization of the polyamide in the non-filled layer
 5 may be lower, if so desired, for instance resulting in a relative viscosity of 1.5. The upper limit of the degree of polymerization is usually determined by the processability of the polyamide and generally corresponds with a relative viscosity of 6.0.

The polyamide for the reinforced and for the non-reinforced layer may contain different additives, depending on its further requirements to be imposed by its application. Such additives may be lubricants,
 10 pigments, colourants, flame retardants, stabilizers, etc. It is advantageous to add additives like pigments, colourants and stabilizers to the non-reinforced polyamide layer only if it is exposed. It is particularly advantageous to incorporate, for instance, metallic additives that serve to provide protection against electromagnetic radiation into the non-reinforced layer only.

Especially for uses for which a high notched impact resistance is required the best results are achieved
 15 if an impact modifier is added to the non-reinforced exposed layer. Impact modifiers known for polyamide applications include carboxylated olefin (co)polymers.

The thickness and number of the various layers of the moulded article according to the invention is not limited. Generally the thickness of the non-filled layers will be lower than that of the filled ones.

The moulded articles according to the invention can be obtained with various processes known per se,
 20 such as injection moulding, moulding, rolling, etc.

The invention will now be further elucidated by means of the following examples without, however, being limited thereto. Polyamide 4,6, STANYL[®], $\eta_{rel} = 3.2$ of DSM, the Netherlands, and Polyamide 6,6, $\eta_{rel} = 2.9$ of Teijin, Japan, are used in the examples.

25 Example I

On test bars obtained by multi-layer injection moulding, with a total thickness of 3.2 mm, the 2.0-mm-thick layer of which contains reinforcing fillers and the outer layers are otherwise non-filled and 0.6 mm
 30 thick, the following characteristics were determined. Table 1 shows the outcome of these measurements.

The test bars showed a smooth surface.

Comparative example 1

Experiments 1 and 7 are repeated, but instead of polyamide 4,6 polyamide 6,6 is used (exp. 9 and 10).
 35 It is clear that rigidity and impact resistance fall short of the experiments in which polyamide 4,6 was used.

Example II and comparative example 2

40 A filled strip of polyamide obtained by extrusion having a thickness of 1.5 mm and a width of 6 cm is hot-pressed with an equally wide 0.5-mm-thick non-filled strip of the same polyamide in a flat shape to form plates of a thickness of about 2.0 mm and 6 x 6 cm. The plates have smooth surfaces.

Of these plates the coefficient of thermal expansion is compared in two directions.

45

50

55

	polyamide	4,6	6,6	4,6
5	filled layer	glass fibre 40% (wt)	glass fibre 40% (wt)	glass fibre/clay 20% (wt)/35% (wt)
10	coefficient of expansion [$\times 10^{-5}/^{\circ}\text{K}$]			
15	machine direction	3	3	3
20	perpendicular to machine direction	6	7	3.5

This clearly shows the superior dimensional stability of the composition according to the invention.

experiment no.	1	2	3	4	5	6	7	8	9	10
non-filled layer	PA46	PA46	PA46	PA46	PA46	PA46	PA46	PA46	PA66	PA66
impact modifier **					10%	10%	20%	20%		20%
filled layer	40%	40%	40%	40%	40%	40%	40%	40%	40%	40%
filler	mica	clay	mixt.	talcum	mica	clay	mica	clay	mica	mica
			glass							
			+ clay*							
Tensile										
modulus *** [MPa]	8075	5000	5760	6060	7775	4700	7350	4470	8450	8030
HDT 1.8 MPa **** [°C]	260	238	264	254	244	220	238	213	226	212
Coeff. of exp.	3	5	3	4	3.5	4	4	4	4.5	5.5
* 10 ⁻⁵ [°K ⁻¹]										
Izod notched ***** [kJ/m ²]	7.5	8	7.5	7	15	14	24	22	4.5	18
impact resistance										

* glass fibre/clay weight ratio = 2 : 3.5

** Keltaflex K 35R a carboxylated EPDM product of DSM, The Netherlands

*** ISO R 527

**** ISO 75

***** ASTM D 256

Claims

Claims for the following Contracting States : AT, BE, CH, DE, FR, GB, GR, IT, LI, NL, SE

- Multi-layer polyamide moulded article comprising a filler-reinforced polyamide layer covered on at least one side with a non-reinforced polyamide layer, characterized in that
 - the polyamide is substantially built up of tetramethylenedipamide units,
 - the filler is predominantly non-fibrous, having a length : width ratio not higher than 10:1.
- Multi-layer polyamide moulded article according to claim 1, characterized in that the filler is chosen from the group of powdery, spherical or plate-shaped particles.
- Multi-layer polyamide moulded part according to claim 1, characterized in that the filler content of the filler-containing layer is between 10 and 80% of the total weight of the layer.
- Multi-layer polyamide moulded article according to claim 3, characterized in that the filler content of the filler containing layer is between 35 and 55% (wt).
- Multi-layer polyamide moulded article according to claim 1, characterized in that the content of tetramethylenedipamide units in the polyamide is at least 75%.
- Multi-layer polyamide moulded article according to claim 5, characterized in that the content of



experiment no.	1	2	3	4	5	6	7	8	9	10
5										
non-filled layer	PA46	PA46	PA46	PA46	PA46	PA46	PA46	PA46	PA66	PA66
impact modifier **					10%	10%	20%	20%		20%
10										
filled layer	40%	40%	40%	40%	40%	40%	40%	40%	40%	40%
filler	mica	clay	mixt.	talcum	mica	clay	mica	clay	mica	mica
			glass							
15			+ clay*							
Tensile										
modulus *** [MPa]	8075	5000	5760	6060	7775	4700	7350	4470	8450	8030
HDT 1.8 MPa **** [°C]	260	238	264	254	244	220	238	213	226	212
20										
Coeff. of exp.	3	5	3	4	3.5	4	4	4	4.5	5.5
* 10 ⁻⁵ [°K ⁻¹]										
Izod notched ***** [kJ/m ²]	7.5	8	7.5	7	15	14	24	22	4.5	18
25										
impact resistance										

* glass fibre/clay weight ratio = 2 : 3.5

** Keltaflex K 35R a carboxylated EPDM product of DSM, The Netherlands

*** ISO R 527

**** ISO 75

***** ASTM D 256

Claims

Claims for the following Contracting States : AT, BE, CH, DE, FR, GB, GR, IT, LI, NL, SE

- Multi-layer polyamide moulded article comprising a filler-reinforced polyamide layer covered on at least one side with a non-reinforced polyamide layer, characterized in that
 - the polyamide is substantially built up of tetramethyleadipamide units,
 - the filler is predominantly non-fibrous, having a length : width ratio not higher than 10:1
- Multi-layer polyamide moulded article according to claim 1, characterized in that the filler is chosen from the group of powdery, spherical or plate-shaped particles.
- Multi-layer polyamide moulded part according to claim 1, characterized in that the filler content of the filler-containing layer is between 10 and 80% of the total weight of the layer.
- Multi-layer polyamide moulded article according to claim 3, characterized in that the filler content of the filler containing layer is between 35 and 55% (wt).
- Multi-layer polyamide moulded article according to claim 1, characterized in that the content of tetramethyleadipamide units in the polyamide is at least 75%.
- Multi-layer polyamide moulded article according to claim 5, characterized in that the content of



tetramethylenedipamide units is at least 85%.

7. Multi-layer polyamide moulded article according to claim 6, characterized in that the polyamide consists of polytetramethylenedipamide homopolymer.
8. Multi-layer polyamide moulded article according to claim 1, characterized in that the degree of polymerization of the polyamide in the filler-containing layer at least results in a relative viscosity of 2.0 measured on a solution of 1 gramme in 100 ml 96%-(wt) sulphuric acid.
9. Multi-layer polyamide moulded article according to claim 1, characterized in that the degree of polymerization of the polyamide in the non-filled layer at least results in a relative viscosity of 1.5.

Claims for the following Contracting State : ES

1. Process for the preparation of multi-layered polyamide articles with a superior combination of physical properties and comprising a filler-reinforced polyamide layer covered on at least one side with a non-reinforced polyamide layer by molding characterized in that
 - a. the polyamide is substantially built up of tetramethylenedipamide units,
 - b. the filler is predominantly non-fibrous, having a length : width ratio not higher than 10:1.
2. Process according to claim 1, characterized in that the filler is chosen from the group of powdery, spherical or plate-shaped particles.
3. Process according to claim 2, characterized in that the filler content of the filler-containing layer is between 10 and 80% of the total weight of the layer.
4. Process according to claim 3, characterized in that the filler content of the filler containing layer is between 35 and 55% (wt).
5. Process according to claim 1, characterized in that the content of tetramethylenedipamide units in the polyamide is at least 75%.
6. Process according to claim 5, characterized in that the content of tetramethylenedipamide units is at least 85%.
7. Process according to claim 6, characterized in that the polyamide consists of poly-tetramethylenedipamide homopolymer.
8. Process according to claim 1, characterized in that the degree of polymerization of the polyamide in the filler-containing layer at least results in a relative viscosity of 2.0 measured on a solution of 1 gramme in 100 ml 96%-(wt) sulphuric acid.
9. Process according to claim 1, characterized in that the degree of polymerization of the polyamide in the non-filled layer at least results in a relative viscosity of 1.5.
10. Process according to claim 1, characterized in that the non-reinforced layer contains one or more substances chosen from the group of colourants, pigments, stabilizers, impact modifiers or additives protecting against electro-magnetic radiation.

Revendications

Revendications pour les Etats contractants suivants : AT, BE, CH, DE, FR, GB, GR, IT, LI, NL, SE

1. Article moulé multicouche en polyamide comprenant une couche de polyamide à remplissage de renforcement recouverte au moins d'un côté d'une couche de polyamide non renforcée, caractérisé en ce que
 - a. le polyamide est essentiellement composé d'unités de tétraméthylène adipamide,
 - b. le matériau de remplissage est en prédominance non fibreux, ayant un rapport longueur:largeur pas plus élevé que 10:1.



2. Article moulé multicouche en polyamide selon la revendication 1, caractérisé en ce que le matériau de remplissage est choisi à partir du groupe de particules en poudre, sphériques ou en forme de plaque.
- 5 3. Article moulé multicouche en polyamide selon la revendication 1, caractérisé en ce que la teneur en matériau de remplissage de la couche contenant le matériau de remplissage est entre 10 et 80 % du poids total de la couche.
- 10 4. Article moulé multicouche en polyamide selon la revendication 3, caractérisé en ce que la teneur en matériau de remplissage de la couche contenant le matériau de remplissage est entre 35 et 55 % (en poids).
5. Article moulé multicouche en polyamide selon la revendication 1, caractérisé en ce que la teneur en unités de tétraméthylène adipamide dans le polyamide est au moins 75 %.
- 15 6. Article moulé multicouche en polyamide selon la revendication 5, caractérisé en ce que la teneur en unités de tétraméthylène adipamide est au moins 85 %.
7. Article moulé multicouche en polyamide selon la revendication 6, caractérisé en ce que le polyamide comprend un homopolymère polytétraméthylène adipamide.
- 20 8. Article moulé multicouche en polyamide selon la revendication 1, caractérisé en ce que le degré de polymérisation du polyamide dans la couche contenant le matériau de remplissage aboutit au moins à une viscosité relative de 2,0 mesurée sur une solution de 1 gramme dans 100 ml d'acide sulfurique à 96 % (en poids).
- 25 9. Article moulé multicouche en polyamide selon la revendication 1, caractérisé en ce que le degré de polymérisation du polyamide dans la couche non remplie aboutit au moins à une viscosité relative de 1,5.

30 **Revendications pour l'Etat contractant suivant : ES**

- 35 1. Procédé pour la préparation d'articles multicouche en polyamide avec une combinaison supérieure des propriétés physiques et comprenant une couche de polyamide renforcée d'un matériau de remplissage recouverte sur au moins un côté d'une couche de polyamide non renforcée par moulage caractérisé en ce que
- a. le polyamide est essentiellement composé d'unités de tétraméthylène adipamide,
- b. le matériau de remplissage est en prédominance non fibreux, ayant un rapport longueur:largeur pas plus élevé que 10:1.
- 40 2. Procédé selon la revendication 1, caractérisé en ce que le matériau de remplissage est choisi à partir du groupe des particules en poudre, sphériques ou en forme de plaque.
3. Procédé selon la revendication 2, caractérisé en ce que la teneur en matériau de remplissage de la couche contenant le matériau de remplissage est entre 10 et 80 % du poids total de la couche.
- 45 4. Procédé selon la revendication 3, caractérisé en ce que la teneur en matériau de remplissage de la couche contenant le matériau de remplissage est entre 35 et 55 % (en poids).
- 50 5. Procédé selon la revendication 1, caractérisé en ce que la teneur en unités de tétraméthylène adipamide dans le polyamide est au moins 75 %.
6. Procédé selon la revendication 5, caractérisé en ce que la teneur en unités de tétraméthylène adipamide est au moins 85 %.
- 55 7. Procédé selon la revendication 6, caractérisé en ce que le polyamide comprend un homopolymère polytétraméthylène adipamide.
8. Procédé selon la revendication 1, caractérisé en ce que le degré de polymérisation du polyamide dans



la couche contenant le matériau de remplissage aboutit au moins à une viscosité relative de 2,0 mesurée sur une solution d'1 gramme dans 100 ml d'acide sulfurique à 96 % (en poids).

9. Procédé selon la revendication 1, caractérisé en ce que le degré de polymérisation du polyamide dans la couche non remplie aboutit au moins à une viscosité relative de 1,5.
10. Procédé selon la revendication 1, caractérisé en ce que la couche non renforcée contient une ou plusieurs substances choisies à partir du groupe des colorants, pigments, stabilisateurs, modificateurs d'impact ou d'additifs protégeant du rayonnement électromagnétique.

Patentansprüche

Patentansprüche für folgende Vertragsstaaten : AT, BE, CH, DE, FR, GB, GR, IT, LI, NL, SE

1. Mehrschichtiger Polyamidformgegenstand umfassend eine füllstoffverstärkte Polyamidschicht, die an mindestens einer Seite mit einer nicht-verstärkten Polyamidschicht überzogen ist, dadurch gekennzeichnet, daß
 - a. das Polyamid im wesentlichen aus Tetramethylenadipamideinheiten aufgebaut ist und
 - b. der Füllstoff überwiegend nicht-faserförmig ist, mit einem Verhältnis Länge : Breite von nicht mehr als 10 : 1.
2. Mehrschichtiger Polyamidformgegenstand nach Anspruch 1, dadurch gekennzeichnet, daß der Füllstoff ausgewählt ist aus der Gruppe von pulverförmigen, sphärischen oder Plättchenförmigen Teilchen.
3. Mehrschichtiger Polyamidformgegenstand nach Anspruch 1, dadurch gekennzeichnet, daß der Füllstoffgehalt der füllstoffhaltigen Schicht 10 bis 80 % des Gesamtgewichtes der Schicht beträgt.
4. Mehrschichtiger Polyamidformgegenstand nach Anspruch 3, dadurch gekennzeichnet, daß der Füllstoffgehalt der füllstoffhaltigen Schicht 35 bis 55 % (Gew.) beträgt.
5. Mehrschichtiger Polyamidformgegenstand nach Anspruch 1, dadurch gekennzeichnet, daß der Gehalt an Tetramethylenadipamideinheiten im Polyamid mindestens 75 % beträgt.
6. Mehrschichtiger Polyamidformgegenstand nach Anspruch 5, dadurch gekennzeichnet, daß der Gehalt an Tetramethylenadipamideinheiten mindestens 85 % beträgt.
7. Mehrschichtiger Polyamidformgegenstand nach Anspruch 6, dadurch gekennzeichnet, daß das Polyamid aus Polytetramethylenadipamidhomopolymer besteht.
8. Mehrschichtiger Polyamidformgegenstand nach Anspruch 1, dadurch gekennzeichnet, daß der Polymerisationsgrad des Polyamids in der füllstoffhaltigen Schicht mindestens zu einer relativen Viskosität von 2,0, gemessen an einer Lösung von 1 g in 100 ml 96 (gew.) %iger Schwefelsäure, führt.
9. Mehrschichtiger Polyamidformgegenstand nach Anspruch 1, dadurch gekennzeichnet, daß der Polymerisationsgrad des Polyamids in der nicht-gefüllten Schicht mindestens zu einer relativen Viskosität von 1,5 führt.

Patentansprüche für folgenden Vertragsstaat : ES

1. Verfahren zur Herstellung von mehrschichtigen Polyamidgegenständen mit einer hervorragenden Kombination von physikalischen Eigenschaften umfassend eine füllstoffverstärkte Polyamidschicht, die an mindestens einer Seite mit einer nicht-verstärkten Polyamidschicht überzogen ist, dadurch gekennzeichnet, daß
 - a. das Polyamid im wesentlichen aus Tetramethylenadipamideinheiten aufgebaut ist und
 - b. der Füllstoff überwiegend nicht-faserförmig ist, mit einem Verhältnis Länge : Breite von nicht mehr als 10 : 1.
2. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß der Füllstoff ausgewählt ist aus der Gruppe von pulverförmigen, sphärischen oder plättchenförmigen Teilchen.



3. Verfahren nach Anspruch 2, dadurch gekennzeichnet, daß der Füllstoffgehalt der füllstoffhaltigen Schicht 10 bis 80 % des Gesamtgewichtes der Schicht beträgt.
- 5 4. Verfahren nach Anspruch 3, dadurch gekennzeichnet, daß der Füllstoffgehalt der füllstoffhaltigen Schicht 35 bis 55 % (Gew.) beträgt.
5. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß der Gehalt an Tetramethylenadipamideinheiten im Polyamid mindestens 75 % beträgt.
- 10 6. Verfahren nach Anspruch 5, dadurch gekennzeichnet, daß der Gehalt an Tetramethylenadipamideinheiten mindestens 85 % beträgt.
7. Verfahren nach Anspruch 6, dadurch gekennzeichnet, daß das Polyamid aus Polytetramethylenadipamidhomopolymer besteht.
- 15 8. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß der Polymerisationsgrad des Polyamids in der füllstoffhaltigen Schicht mindestens zu einer relativen Viskosität von 2,0, gemessen an einer Lösung von 1 g in 100 ml 96 (gew.) %iger Schwefelsäure, führt.
- 20 9. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß der Polymerisationsgrad des Polyamids in der nicht-gefüllten Schicht mindestens zu einer relativen Viskosität von 1,5 führt.
- 25 10. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß die nicht-verstärkte Schicht eine oder mehrere Substanzen ausgewählt aus der Gruppe der Farbstoffe, Pigmente, Stabilisatoren, Schlagmodifikatoren oder Schutzadditive gegen elektromagnetische Strahlung enthält.

30

35

40

45

50

55