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PARTIALLY AROMATIC COPOLYAMIDES

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(56) Prior Art Documents
US 4018746
US 5028462
US 5612446

(57) Claim

1. A partially aromatic copolyamide having metaxylylene diamine and hexamethylene diamine as the amine components and adipic acid and at least one further dicarboxylic acid selected from the group of aliphatic dicarboxylic acids with 7 to 10 carbon atoms as well as further additives, if required, wherein the copolyamide includes the following components:

a. 5 to 30 weight-% of hexamethylene diamine
b. 10 to 40 weight-% of metaxylylene diamine
c. 15 to 50 weight-% of adipic acid
d. 5 to 45 weight-% of at least one aliphatic dicarboxylic acid with 7 to 10 carbon atoms,

wherein the components a. to d. add up to 100 weight-%, and the acid groups and the amine groups are present in approximately equi-molar portions.

12. Use of the copolyamide in accordance with any one of claims 8 to 11, wherein said multilayer composite is selected from the group consisting of foils, containers, infusion- or ostomy bags, shrink wraps for meat, fish and cheese packagings and mono- or multi-layered sausage casings.

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14. A mono- or multi-layered packaging, containing at least one barrier layer made of a partially aromatic copolyamide in accordance with any one of claims 1 to 5 and/or at least one barrier layer made of mixtures of the partially aromatic copolyamide in accordance with any one of claims 1 to 5 with other thermoplastic polymers.

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Patents Act

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COPOLYAMIDES

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The following statement is a full description of this invention, including the best method of performing it known to applicant(s):

FIELD OF THE INVENTION

The invention relates to a partially aromatic copolyamide based on metaxylylene diamine and hexamethylene diamine as the amine components and adipic acid and at least one further dicarboxylic acid selected from the group of aliphatic dicarboxylic acids with 7 to 10 carbon atoms as well as further additives, if required.

BACKGROUND OF THE INVENTION

Materials made of partially aromatic, generally partially crystalline, copolyamide show a special combination of mechanical properties (toughness and flexibility, among others), thermal properties (such as melting point and ability to be sterilized, among others) and barrier effects.

An increasing requirement for suitable plastic materials to replace glass and metal containers has existed for a long time in the packaging and food industry as well as in the pharmaceutical industry. This applies in particular to foodstuffs, beverages and pharmaceutical products. As a rule the multilayered packaging systems employed in these areas comprise several layers of different polymers, such as polyethylene, polypropylene, polyvinyl-chloride and -fluoride, polyvinyl alcohol, polyacrylate and other polymers, their blends and their mixtures.

The above mentioned packaging systems are intended to protect foodstuffs, beverages and medical, chemical, biological and pharmaceutical products. In the widest sense these packaging systems include hoses, tubes, bottles, containers, packaging foils and the like.

However, it is a requirement for the above mentioned areas of applications that the plastic materials used have barrier layer effects in respect to gases such as oxygen, carbon dioxide, water vapor and other gases, in addition to good working properties and good mechanical properties. It is also intended to provide a barrier against flavorings and fragrances or toxic and/or non-toxic gases.

Many lactam-containing copolyamides have been described so far in the patent literature, which have the disadvantage that monomers migrate out of the copolyamide layer, which is impermissible and dubious for toxicological reasons in connection with packaging in the area of foodstuffs.

Copolyamides with metaxylylene diamine (MXDA) as components have quite often been described, for example in EP-A-411 791, EP-A-288 972, GB-A-1,575,801, JP-A-01 319531, JP-A-02 089643, JP 05 064866, JP 52-135352 with aromatic dicarboxylic acids, mainly isophthalic acid and terephthalic acid as the comonomers. Based on the required high condensation temperatures and the occurring high melt viscosities, copolyamides of this type are difficult to produce. The resulting materials have very high stiffness and brittleness.

Copolyamides with MXDA and caprolactam, such as have been described in DE-AS-18 12 018, JP 52-135353, US-A 4,826,955 and WO 93/21276, must be extracted for use in the packaging field to reduce the migration of the lactam residue. The additional extraction step lowers the profitability of the material. Nevertheless, the materials obtained do not satisfy all requirements, for example in the medical sector.

Copolyamides made of MXDA and dimeric fatty acids have been described in EP-A-355 017 and JP-A-05 295313. Because of the long carbon chains of the fatty acid components, copolyamides of this composition show insufficient barrier properties against gases.

OBJECT AND SUMMARY OF THE INVENTION

It is therefore the object of the invention to make available copolyamides containing metaxylylene diamine (MXDA) as a monomer component for use as barrier layer in multi-layered packaging materials, which overcome or at least alleviate one or more of the disadvantages of the prior art mentioned above.

Copolyamide compositions of metaxylylene diamine (MXDA) and at least three further monomers and their use as a barrier layer in multilayered composites are a particular object of the invention.

Copolyamides of MXDA and hexamethylene diamine (HMDA) as the amino component as well as adipic acid and at least a further dicarboxylic acid selected from the group of the aliphatic dicarboxylic acids with 7 to 10 carbon atoms are materials which do not have the disadvantages mentioned.

A combination of the following components is provided in

accordance with the invention:

a. 5 to 30 weight-% of HMDA

b. 10 to 40 weight-% of MXDA

c. 15 to 50 weight-% of adipic acid

d. 5 to 45 weight-% of at least one further aliphatic dicarboxylic acid with 7 to 10 atoms.

The monomer portions a. to d. add up to 100 weight-%, wherein the amine and acid components are present in approximately equi-molar portions.

It is known to one skilled in the art that, for generating defined polymerization degrees or end groups or for reasons of production technology, in the course of polyamide production the amine or the acid components are employed at a slight excess, as a rule not more than 5 mol-%.

A particularly preferred composition in accordance with the invention includes

a. 8 to 27 weight-% of HMDA

b. 13 to 39 weight-% of MXDA

c. 19 to 47 weight-% of adipic acid

d. 7 to 41 weight-% of sebacic acid or azelaic acid or a mixture thereof,

wherein the monomer portions a. to d. add up to 100 weight-%.

The partially aromatic copolyamides in accordance with the invention may contain the usual additives in accordance with the prior art, such as chain regulators (preferably amines or diamines), stabilizers, anti-foaming agents, crystallization accelerators, and the like.

The production of the partially aromatic copolyamides in accordance with the invention is performed in a known manner in accordance with the melt condensation process.

Depending on the application, the preferred range of the relative viscosity of the copolyamide in accordance with the invention (measured as a 0.5% solution in m-cresol at 20°C) lies between 1.6 and 2.5. However, higher as well as lower viscosities can also be produced without problems.

Several, if required different, barrier layers and several further polymer layers can be used for the multilayered composites. Preferred further polymer layers are protective and support layers which give the multilayered composite defined application properties. Sealing layers are required to be used to make the multilayered composite sealable by hot sealing. Coupling agent layers can also be used advantageously.

Preferred polymers for the protective and support layers are those consisting of polyamides, polyolefins or polyesters.

Preferred coupling agent layers are functionalized polyolefins, i.e. polyolefins provided with functional groups.

Sealing layers advantageously consist of low-melting polymers. So-called inomers, besides polyolefins, are preferred.

The production of the multilayered composite is advantageously performed in coextrusion installations, but can also be performed by means of laminating.

Areas of use of the partially aromatic copolyamides in accordance with the invention are found in multilayered composites for, among others, the medical area, for example as the only or an additional barrier layer in infusion and ostomy bags or in shrink wraps for meat, fish and cheese packaging or sausage casings.

The use as a blend component for mixtures with ethylene vinyl alcohols should be mentioned as a special use, which serves to improve the deep-drawing properties and the flexibility of the ethylene vinyl alcohols and which involves a relatively small loss in the barrier effect. Blends of this type can be used for producing containers.

A further option is provided by the use of the copolyamides in accordance with the invention for producing mono- and multi-layered sausage skins. For this purpose the partially aromatic copolyamide in accordance with the invention can be used in pure form or in a mixture with other polymers, for example polyamides, preferably polyamide 6.

The copolyamides in accordance with the invention can be employed in the non-oriented or the uniaxially or biaxially oriented state for all areas of application.

Sterilization of the copolyamides in accordance with the invention is also possible, in part without loss of the mechanical properties and with only very slight loss of transparency.

The copolyamides of the present invention have the advantage of

a high melt viscosity,

a great stiffness, and

a great brittleness while avoiding

the necessity of

a high condensation temperatures and

an additional extraction step.

In this regard the combination of mechanical properties, thermal properties and barrier effect are particularly advantageous.

The invention will be explained by means of the following example.

DETAILED DESCRIPTION

An autoclave which is well agitable is charged with monomers corresponding to the composition of Table 1. A pressure of 18 to 20 bar is built up in the pressure phase at a temperature of approximately 270°C. This is let off in the subsequent expansion phase. The final polycondensation takes place in the degassing step which follows. The temperature of the melt should not exceed 275°C. The entire process lasts between 6 and 9 hours.

The product is delivered in the form of a strand by means of a melt pump, cooled in a water bath, granulated and subsequently dried.

Table 1

Composition by Weight-%

	HMDA	MXDA	Adipic Acid	Sebacic Acid
Example	24,28	18,97	35,63	21,12

The properties of the partially aromatic copolyamide in accordance with the invention as well as the properties of the copolyamide foils produced in a foil extruder are shown in tables 2 and 3.

The oxygen and carbon dioxide permeations represented in Table 3 were measured with a gas permeability testing device in accordance with the DIN 53380 (ISO 2556) standard.

Furthermore, the tensile strength of the blown films in accordance with the invention (50 mm) was measured in accordance with ISO 1184 traverse to the direction of the machine. In the process, values between 60 to 80 N/mm² were measured for the copolyamide foils in accordance with the invention.

Table 2

Properties

Melt Viscosity (275°C/5kg)	[Pa s]	100-600
Impact, notched Charpy, 23°C **	[kJ/m²]	*
Tensile E-Modulus **	[N/mm²]	500
TG DSC (Inflection Point)	[°C]	57
Melting Point	[°C]	181

* Test rods without breaking (in accordance with DIN 53453)

** Measured on conditioned test bars

Table 3

Properties

Blown Film of 50 µm Thickness		
Permeation	[cm^3 /m^2 d bar]	
Oxygen	0% rh	50
	85% rh	20
Carbon Dioxide	0% rh	140
	85% rh	190

Permeation: Measuring Devices 0% rh Lissy L 100

85% rh Mocon Oxtran Twin

rh = relative humidity

The claims defining the invention are as follows:

1. A partially aromatic copolyamide having metaxylylene diamine and hexamethylene diamine as the amine components and adipic acid and at least one further dicarboxylic acid selected from the group of aliphatic dicarboxylic acids with 7 to 10 carbon atoms as well as further additives, if required, wherein the copolyamide includes the following components:

a. 5 to 30 weight-% of hexamethylene diamine
b. 10 to 40 weight-% of metaxylylene diamine
c. 15 to 50 weight-% of adipic acid
d. 5 to 45 weight-% of at least one aliphatic dicarboxylic acid with 7 to 10 carbon atoms,

wherein the components a. to d. add up to 100 weight-%, and the acid groups and the amine groups are present in approximately equi-molar portions.

2. A copolyamide in accordance with claim 1, wherein the copolyamide includes

a. 8 to 27 weight-% of hexamethylene diamine
b. 13 to 39 weight-% of metaxylylene diamine
c. 19 to 47 weight-% of adipic acid
d. 7 to 41 weight-% of at least one aliphatic dicarboxylic acid with 7 to 10 carbon atoms,

wherein the components a. to d. add up to 100 weight-%, and the acid groups and the amine groups are present in approximately equi-molar portions.

3. A copolyamide in accordance with claim 1 or claim 2, wherein said aliphatic dicarboxylic acid is sebacic acid or acelaic acid or a mixture thereof.

4. A copolyamide in accordance with claim 1 and 2, consisting of approximately 24 weight-% of hexamethylene diamine, approximately 19 weight-% of metaxylylene diamine, approximately 35 weight-% of adipic acid and approximately 21 weight-% of sebacic acid.

5. A copolyamide in accordance with any one of the preceding claims, having a relative viscosity (measured as a 0.5% solution in m-cresol at 20°C) of between 1.6 and 2.5.

6. Use of the copolyamide in accordance with any one of the preceding claims for producing blends with other thermoplastic

polymers.

7. Use of the copolyamide in accordance with claim 6, wherein said other thermoplastic polymers are ethylene vinyl alcohol polymers.

8. Use of the copolyamide in accordance with any one of the preceding claims for producing barrier layers for multilayered composites.

9. Use of the copolyamide in accordance with claim 8, wherein the copolyamide is present in its pure form.

10. Use of the copolyamide in accordance with claim 8, wherein the copolyamide is present as a mixture with other polymers.

11. Use of the copolyamide in accordance with claim 8, wherein the copolyamide is present in combination with one or more other polymer layers.

12. Use of the copolyamide in accordance with any one of claims 8 to 11, wherein said multilayer composite is selected from the group consisting of foils, containers, infusion- or ostomy bags, shrink wraps for meat, fish and cheese packagings and mono- or multi-layered sausage casings.

13. A barrier layer made of partially aromatic copolyamide, in particular for multilayered packagings, wherein the barrier layer is transparent and the copolyamide is a partially aromatic copolyamide in accordance with any one of claims 1 to 5.

14. A mono- or multi-layered packaging, containing at least one barrier layer made of a partially aromatic copolyamide in accordance with any one of claims 1 to 5 and/or at least one barrier layer made of mixtures of the partially aromatic copolyamide in accordance with any one of claims 1 to 5 with other thermoplastic polymers.

15. A packaging in accordance with claim 14, wherein said other thermoplastic polymers are ethylene vinyl alcohol polymers.

16. A packaging in accordance with claim 14 or claim 15, containing in addition to the at least one barrier layer further polymer layers.

17. A packaging in accordance with claim 16, wherein said further polymer layers are selected from the group consisting of support layers, protection layers, sealing layers and

coupling agent layers.

18. A packaging in accordance with claim 17, wherein the polymers or the polymer layers are selected from the group consisting of polyvinyl alcohol, polyacrylate, polyolefin, polyester, copolyester, polyamide, copolyamide, polycarbonate or other polymers, their blends or their mixtures.

19. A packaging in accordance with any one of claims 14 to 18, having a single barrier layer made of mixtures of the partially aromatic copolyamide in accordance with any one of claims 1 to 5 with other polymers.

20. A packaging in accordance with claim 19, wherein said other polymers are polyamides.

21. A packaging in accordance with claim 20, wherein said polyamide is polyamide 6.

22. A packaging in accordance with any one of claims 14 to 21, produced by means of coextrusion or blow molding or injection stretch blow molding, optionally in combination with deep drawing.

23. A partially aromatic copolyamide in accordance with claim 1 substantially as hereinbefore described with reference to the example.

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ABSTRACT

The invention relates to novel partially aromatic copolyamides having metaxylylene diamine and hexamethylene diamine as the amine components and adipic acid and at least one further dicarboxylic acid selected from the group of aliphatic dicarboxylic acids with 7 to 10 carbon atoms as well as further additives, if required, wherein the copolyamide includes the following components:

a. 5 to 30 weight-% of hexamethylene diamine
b. 10 to 40 weight-% of metaxylylene diamine
c. 15 to 50 weight-% of adipic acid
d. 5 to 45 weight-% of at least one aliphatic dicarboxylic acid with 7 to 10 carbon atoms, preferably sebacic acid and/or acelaic acid,

wherein the components a. to d. add up to 100 weight-%, and the acid groups and the amine groups are essentially present in equi-molar portions. These novel copolyamides are used for producing barrier layers for mono- or multi-layered composites, such as foils or containers, infusion- or ostomy bags, shrink wraps for meat, fish and cheese packagings or sausage casings, wherein the copolyamides can be present in the pure form or as a mixture with other polymers, in particular in combination with further polymer layers.