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(54) **COMPOSITE MULTICOUCHE**
(54) **MULTILAYER COMPOSITE**

(57) A thermoplastic multilayer composite which comprises the following layers: I. a layer I of a thermoplastic molding composition; II. a layer II of a further thermoplastic molding composition; in between a layer of an adhesion promoter which comprises at least 5% by weight of a graft copolymer prepared using the following monomers: a) from 0.5 to 25% by weight, based on the graft copolymer, of a polyamine having at least 4 nitrogen atoms and having a number average molecular weight M_n of at least 146 g/mol, and b) polyamide-forming monomers selected from lactams, ω-aminocarboxylic acids and/or equimolar combinations of diamine and dicarboxylic acid, has good layer adhesion.

Abstract:

A thermoplastic multilayer composite which comprises the following layers:

I. a layer I of a thermoplastic molding composition;
II. a layer II of a further thermoplastic molding composition;

in between a layer of an adhesion promoter which comprises at least 5% by weight of a graft copolymer prepared using the following monomers:

a) from 0.5 to 25% by weight, based on the graft copolymer, of a polyamine having at least 4 nitrogen atoms and having a number average molecular weight M_n of at least 146 g/mol, and

b) polyamide-forming monomers selected from lactams, ω-aminocarboxylic acids and/or equimolar combinations of diamine and dicarboxylic acid,

has good layer adhesion.

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Multilayer Composite

FIELD OF THE INVENTION

The invention relates to an adhesion promoter for a multilayer composite, and to a multilayer composite which contains this adhesion promoter.

BACKGROUND OF THE INVENTION

Individual polymers, such as, for example, polyamides or polyesters, are unsuitable for many applications on their own. Thus, for example, polyamides are not resistant to weathering since they age on exposure and absorb atmospheric moisture. This results in discoloration, impairment of the mechanical properties and warping phenomena.

Although polyamides have good mechanical properties, in particular good toughness, they have a poor barrier action. Polar substances in particular can easily migrate through polyamides. This is extremely disadvantageous, for example, in fuel lines in which alcohol-containing fuel is conveyed.

Polyesters generally have good weathering resistance and an excellent barrier action both to polar and to non-polar media. However, they are generally impact-sensitive; the notched impact strength in particular is frequently inadequate in polyesters. Polyesters therefore cannot be used alone in many cases in which other properties, such as their excellent barrier action, high heat resistance and good rigidity, would in fact be desired.

Other polymers, too, generally exhibit an unbalance property profile and are therefore unsuitable for many applications.

It would therefore be desirable to produce a strong bond between different polymers, for example between polyamide and polyester. It would thus be possible, for example, to protect polyamide moldings against light and humidity by coating with polyester. In exactly the same way, a polyester molding could be protected against chemical and mechanical influences by coating with polyamide. Furthermore, it would thus be possible to provide fuel lines, which usually consist of a polyamide (PA), such as PA 6, PA 11 or PA 12, with a barrier layer to fuel, in particular to alcohol-containing fuel. On the other hand, laminates comprising various layers having different functions are more suitable than monolayers for food packaging.

Composites of polyamide and polyester are already known in principle. European Patent Publication No. (EP-A)-0 336 806 describes the coextrusion of PA 12 and polybutylene terephthalate (PBT) to give a two-layer pipe. German Patent No. 38 27 092 describes a multilayer pipe which has, from the inside outward, layers of polyamide, polyvinyl alcohol, polyamide and polyester. However, it is known to the person skilled in the art that by far the majority of polymers, including polyamides and polyesters, are incompatible with one another, which is why adhesion is not achieved between the laminate layers during the production of polymer laminates. However, a strong bond between the individual polymer layers is absolutely necessary in the usual industrial applications.

German Patent Publication No. (DE-A) 196 33 133 describes a multilayer pipe comprising at least two layers bonded well to one another, where the first layer is a barrier layer and the thermoplastic of the second layer has been treated with polyethyleneimine as adhesion promoter. On reworking German Patent Publication No. (DE-A) 196 33 133, however, the desired effect does not occur.

It would per se be obvious to bond, for example, polyester and polyamide layers by means of an adhesion promoter consisting of a mixture of polyamide and polyester. However, blends of this type, which are usually prepared by mixing the melts in an extruder, are very brittle. Corresponding coextrusion experiments on polyamide and polyester either exhibit adhesion to the polyamide or to the polyester, but never to the two polymers simultaneously.

European Patent Publication No. (EP-A)-0 509 211 describes thermoplastic multilayer composites in which a layer of a polyamide molding composition and a layer of a polyester molding composition are bonded by means of an adhesion promoter which comprises a mixture of polyamide and polyester. Since the problems discussed above occur here, in a preferred embodiment at least part of the polyamide content and of the polyester component in the adhesion promoter are in the form of a polyamide-polyester block copolymer. However, the preparation of block copolymers of this type is not entirely simple and requires the addition of auxiliaries or catalysts. Furthermore, precise monitoring of the end groups is necessary since the block copolymers are prepared by linking suitable end groups and it must therefore be ensured that the appropriate end groups are present in sufficient concentration. Since commercial products have not been matched to these requirement, specialty grades must be prepared and subsequently converted into a block copolymer. The production of adhesion promoters of this type is therefore associated with considerable effort. This is more particularly true of the block copolyester-amides employed in the process of European Patent Publication No. (EP-A)-0 837 088 as adhesion promoters in polyamide-polyester multilayer composites.

Composites comprising other materials are likewise known. Owing to the incompatibility of most polymer materials,

however, special solutions with individually matched adhesion promoters are usually required.

SUMMARY OF THE INVENTION

A major object of the invention is to provide an inexpensive, easy-to-prepare, but nonetheless effective adhesion promoter for a multilayer composite. In a multilayer composite of this type, the layer adhesion is desired to remain for a long time, even in contact with reagents such as, for example, fuel, solvents, oil or greases and at elevated temperature.

In one aspect, the invention provides a thermoplastic multilayer composite comprising a layer I of a thermoplastic molding material, a layer II of another thermoplastic molding material and, between layer I and layer II, a layer of an adhesion promoter which comprises at least 5% by weight, preferably at least 10% by weight and particularly preferably at least 20% by weight of a graft copolymer comprising the following monomers:

a) from 0.5 to 25% by weight, preferably from 1 to 20% by weight and particularly preferably from 1.5 to 16% by weight, based on the graft copolymer, of a polyamine having at least 4, preferably at least 8 and particularly preferably at least 11 nitrogen atoms and having a number average molecular weight M_n of at least 146, preferably of at least 500 and particularly preferably of at least 800, and

b) a polyamide-forming monomer selected from the group consisting of lactams, ω-aminocarboxylic acids, and equimolar combinations of a diamine and a dicarboxylic acid.

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DESCRIPTION OF PREFERRED EMBODIMENTS

In a preferred embodiment, the amino group concentration of the graft copolymer is in the range from 100 to 2500 mmol/kg.

The polyamine used can be, for example, the following classes of substance:

- polyvinylamines (Römpp Chemie Lexikon [Römpp's Lexicon of Chemistry], 9th Edition, Volume 6, page 4921, Georg Thieme Verlag, Stuttgart, 1992)

- polyamines prepared from alternating polyketones (DE-A 196 54 058)

- dendrimers, such as, for example, $((H_2N\text{-}(CH_2)_3)_2N\text{-}(CH_2)_3)_2\text{-}N(CH_2)_2\text{-}N((CH_2)_2\text{-}N((CH_2)_3\text{-}NH_2)_2)_2$ (DE-A 196 54 179) or tris(2-aminoethyl)amine, N,N-bis(2-aminoethyl)-N',N'-bis[2-[bis(2-aminoethyl)amino]ethyl]-1,2-ethanediamine or 3,15-bis(2-aminoethyl)-6,12-bis[2-[bis(2-aminoethyl)amino]ethyl]-9-[2-[bis[2-bis(2-aminoethyl)amino]ethyl]amino]ethyl]-3,6,9,12,15-pentaazaheptadecane-1,17-diamine (J.M. Warakomski, Chem. Mat. 1992, 4, 1000 – 1004);

- linear polyethyleneimines, which can be prepared by polymerization of 4,5-dihydro-1,3-oxazoles followed by hydrolysis (Houben-Weyl, Methoden der Organischen Chemie [Methods of Organic Chemistry], Volume E20, pages 1482 - 1487, Georg Thieme Verlag, Stuttgart, 1987);

- branched polyethyleneimines, which are obtainable by polymerization of aziridines (Houben-Weyl, Methoden der Organischen Chemie [Methods of Organic Chemistry], Volume E20, pages 1482 - 1487, Georg Thieme Verlag, Stuttgart, 1987) and which generally have the following amino group distribution:
from 25 to 46% of primary amino groups,
from 30 to 45% of secondary amino groups and
from 16 to 40% of tertiary amino groups.

In the preferred case, the polyamine has a number average molecular weight M_n of at most 20,000 g/mol, particularly preferably of at most 10,000 g/mol and especially preferably of at most 5000 g/mol.

Lactams and ω-aminocarboxylic acids which are employed as polyamide-forming monomers contain from 4 to 19 and in particular from 6 to 12 carbon atoms. Particular preference is given to ε-caprolactam, ε-aminocaproic acid, caprylolactam, ω-aminocaprylic acid, laurolactam, ω-aminododecanoic acid and/or ω-aminoundecanoic acid.

Combinations of diamine and dicarboxylic acid are, for example, hexamethylenediamine/adipic acid, hexamethylenediamine/dodecanedioic acid, octamethylenediamine/sebacic acid, decamethylenediamine/sebacic acid, decamethylenediamine/dodecanedioic acid, dodecamethylene-diamine/dodecanedioic acid and dodecamethylenediamine/2,6-naphthalenedicarboxylic acid. In addition, however, it is also possible to employ all other combinations, such as decamethylenediamine/dodecanedioic acid/terephthalic acid, hexamethylenediamine/adipic acid/terephthalic acid, hexamethylene-diamine/adipic acid/caprolactam, decamethylenediamine/dodecanedioic acid/ω-aminoundecanoic acid, decamethylenediamine/dodecanedioic acid/laurolactam, decamethylenediamine/terephthalic acid/laurolactam or dodecamethylenediamine/2,6-naphthalenedicarboxylic acid/laurolactam.

In a preferred embodiment, the graft copolymer is prepared with the additional use of an oligocarboxylic acid selected from 0.015 to about 3 mol% of dicarboxylic acid and 0.01 to about 1.2 mol% of tricarboxylic acid, in each case based on the sum of the other polyamide-forming monomers. In this connection, each monomer in the equivalent combination of diamine and dicarboxylic acid is considered individually. In this way, the polyamide-forming monomers have in total a slight excess of carboxyl groups. If a dicarboxylic acid is used, preferably from 0.03 to 2.2 mol%, particularly preferably from 0.05 to 1.5 mol%, very particularly preferably from 0.1 to 1 mol% and in particular from 0.15 to 0.65 mol% is added; if a tricarboxylic acid is used, preferably from 0.02 to 0.9 mol%, particularly preferably from 0.025 to 0.6 mol%, very particularly preferably from 0.03 to 0.4 mol% and in particular from 0.04 to 0.25 mol% is used. The concomitant use of the oligocarboxylic acid significantly improves the solvent and fuel resistance, in particular the hydrolysis and alcoholysis

resistance and the stress cracking resistance, but also the swelling behavior and consequently the dimensional stability, as well as the diffusion barrier action.

The oligocarboxylic acid employed can be any desired di- or tricarboxylic acid having 6 to 24 carbon atoms, for example adipic acid, suberic acid, azelaic acid, sebacic acid, dodecanedioic acid, isophthalic acid, 2,6-naphthalenedicarboxylic acid, cyclohexane-1,4-dicarboxylic acid, trimesic acid and/or trimellitic acid.

In addition, if desired, aliphatic, alicyclic, aromatic, aralkylic and/or alkylaryl-substituted monocarboxylic acids having 3 to 50 carbon atoms, such as, for example, lauric acid, unsaturated fatty acids, acrylic acid or benzoic acid, can be employed as regulator. By means of these regulators, the concentration of amino groups can be reduced without changing the shape of the molecule. In addition, functional groups, such as double or triple bonds, etc., can be introduced in this way. However, it is desired that the graft copolymer has a substantial content of amino groups. The amino group concentration of the graft copolymer is preferably in the range from 150 to 1500 mmol/kg, particularly preferably in the range from 250 to 1300 mmol/kg and very particularly preferably in the range from 300 to 1100 mmol/kg. Here and below, the term "amino groups" is taken to mean not only amino end groups, but also any secondary or tertiary amine functions which may be present in the polyamine.

The graft copolymers according to the invention can be prepared by various processes.

One possibility is to initially introduce the lactam or ω-aminocarboxylic acid and polyamine together and to carry out the polymerization or polycondensation. The oligocarboxylic acid can be added either at the beginning or during the reaction.

However, a preferred process comprises, in a two-step process, firstly carrying out the lactam cleavage and prepolymerization in the presence of water (alternatively, the corresponding ω-aminocarboxylic acids or diamines and dicarboxylic acids are employed and prepolymerized directly); in the second step, the polyamine is added, while any oligocarboxylic acid used concomitantly is metered in before, during or

after the prepolymerization. The mixture is then decompressed at temperatures of from 200 to 290°C and polycondensed in a stream of nitrogen or under reduced pressure.

A further preferred process comprises the hydrolytic degradation of a polyamide to a prepolymer and the simultaneous or subsequent reaction with the polyamine. Preference is given to polyamides in which the end group difference is approximately zero or in which any oligocarboxylic acid used concomitantly has already been copolycondensed. However, the oligocarboxylic acid can also be added at the beginning or during the degradation reaction.

These processes allow the preparation of ultra-highly branched polyamides having acid numbers of less than 40 mmol/kg, preferably less than 20 mmol/kg and particularly preferably less than 10 mmol/kg. After a reaction time of only from one to five hours at temperatures of from 200°C to 290°C, approximately complete conversion is achieved.

If desired, this can be followed, in a further process step, by a multi-hour vacuum phase. This lasts at least four hours, preferably at least six hours and particularly preferably at least eight hours at from 200 to 290°C. After an induction period of several hours, an increase in the melt viscosity is then observed, which is probably attributable to a reaction of amino end groups taking place with one another with elimination of ammonia and with chain linking. This further increases the molecular weight, which is particularly advantageous for extrusion molding compositions.

If it is not desired to continue the reaction to completion in the melt, the ultra-highly branched polyamide can also be post-condensed in the solid phase in accordance with the prior art.

By means of this adhesion promoter, a multiplicity of polymers or molding compositions based thereon can be bonded to one another. In general, suitable polymers are all those which, owing to structural similarity, are physically compatible with the graft copolymer used in accordance with the invention, such as, for example, polyamides. Equally suitable are all polymers which undergo a chemical linking reaction or at least form hydrogen bonds with the amino groups of the graft copolymer, such as, for example, polyesters.

Embodiments according to the invention are, for example:

- A multilayer composite which comprises layers of different polyamide molding compositions which are of low compatibility or are incompatible with one another and which are bonded by means of the adhesion promoter according to the invention.

- A multilayer composite which comprises layers of different polyester molding compositions which are incompatible with one another and are bonded by the adhesion promoter according to the invention.

- A multilayer composite which comprises a layer of a polyamide molding composition which is bonded, by means of the adhesion promoter according to the invention, to a layer of another molding composition which is based on a polymer which is not a polyamide.

- A multilayer composite which comprises a layer of a polyester molding composition which is bonded, by means of the adhesion promoter according to the invention, to a layer of another molding composition which is based on a polymer which is not a polyester.

- A multilayer composite which comprises the following layers:
  I. A layer I of a polyamide molding composition;
  II. A layer II of a polyester molding composition;
  in between a layer of the adhesion promoter according to the invention.

Suitable polyamides here are primarily aliphatic homo- and copolycondensates, for example PA 46, PA 66, PA 68, PA 612, PA 88, PA 810, PA 1010, PA 1012, PA 1212, PA 6, PA 7, PA 8, PA 9, PA 10, PA 11 and PA 12. (The notation of the polyamides corresponds to the international standard, where the first number(s) indicates the number of carbon atoms in the starting diamine and the final number(s) denotes the number of carbon atoms in the dicarboxylic acid. If only one number is given, this means that the starting material was an α,ω-aminocarboxylic acid or the lactam derived therefrom; for more information, see H. Domininghaus, Die Kunststoffe und ihre Eigenschaften [The Plastics and Their Properties], pages 272 ff., VDI-Verlag, 1976.)

If copolyamides are used, these can contain, for example, adipic acid, sebacic acid, suberic acid, isophthalic acid, terephthalic acid, naphthalene-2,6-dicarboxylic acid, etc., as co-acid or bis(4-amino-cyclohexyl)methane, trimethylhexamethylenediamine, hexamethylenediamine or the like as co-diamine. Lactams, such as caprolactam or laurolactam, or aminocarboxylic acids, such as ω-aminoundecanoic acid, can likewise be incorporated as co-component.

The preparation of these polyamides is known (for example D.B. Jacobs, J. Zimmermann, Polymerization Processes, pp. 424 - 467, Interscience Publishers, New York, 1977; DE-B 21 52 194).

In addition, suitable polyamides are also mixed aliphatic/aromatic polycondensates, as described, for example, in US Patents 2,071,250, 2,071,251, 2,130,523, 2,130,948, 2,241,322, 2,312,966, 2,512,606 and 3,393,210, and in Kirk-Othmer, Encyclopedia of Chemical Technology, 3rd Edn, Vol. 18, pages 328 ff. and 435 ff., Wiley & Sons, 1982. Other suitable polyamides are poly(ether-ester-amides) and poly(ether-amides); products of this type are described, for example, in DE-A 25 23 991, 27 12 987 and 30 06 961.

The polyamide molding composition can comprise either one of these polyamides or a plurality in the form of a mixture. Furthermore, up to 40% by weight of other thermoplastics may be present so long as they do not adversely affect the bonding ability, in particular impact-modifying rubbers, such as ethylene-propylene or ethylene-propylene-diene copolymers (EP-A-0 295 076), polypentenylene, polyoctenylene, random or block copolymers of alkenyl-aromatic compounds with aliphatic olefins or dienes (EP-A-0 261 748) or core/shell rubbers having a tough, elastic core of (meth)acrylate, butadiene or styrene-butadiene rubber having glass transition temperatures T_g of < -10°C, where the core may be crosslinked and the shell may be built up from styrene and/or methyl methacrylate and/or further unsaturated monomers (DE-A 21 44 528 and 37 28 685).

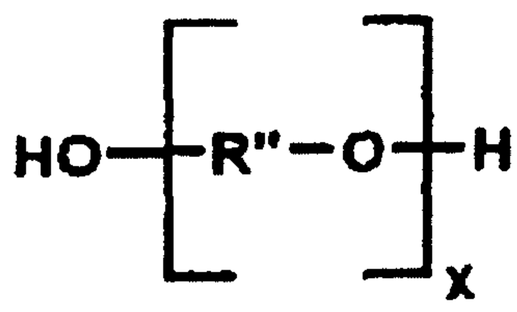
The conventional auxiliaries and additives for polyamides, such as, for example, flame retardants, stabilizers, plasticizers, processing auxiliaries, fillers, in particular for improving the electrical conductivity, reinforcing fibers, pigments or the like, can be added to the polyamide molding

composition. The amount of said agents should be metered in such a way that the desired properties are not seriously impaired.

Suitable polyesters are thermoplastic polyesters having a linear structure. These are prepared by polycondensation of diols with dicarboxylic acid or polyester-forming derivatives thereof, such as dimethyl esters. Suitable diols have the formula HO-R-OH, where R is a divalent, branched or unbranched, aliphatic and/or cycloaliphatic radical having 2 to 40, preferably 2 to 12, carbon atoms. Suitable dicarboxylic acids have the formula HOOC-R'-COOH, where R' is a divalent aromatic radical having 6 to 20, preferably 6 to 12, carbon atoms.

Examples of diols which may be mentioned are ethylene glycol, trimethylene glycol, tetramethylene glycol, hexamethylene glycol, neopentyl glycol, cyclohexanedimethanol and the C_{36}-diol dimer diol. The diols can be employed alone or as a diol mixture.

Up to 25 mol% of said diol may be replaced by a polyalkylene glycol having the following general formula:



where R" is a divalent radical having 2 to 4 carbon atoms, and x can adopt a value of from 2 to 50.

Examples of suitable aromatic dicarboxylic acids are terephthalic acid, isophthalic acid, 1,4-, 1,5-, 2,6- and 2,7-naphthalenedicarboxyic acid, diphenic acid and 4,4'-oxybis(benzoic acid). Up to 30 mol% of these dicarboxylic acids may be replaced by aliphatic or cycloaliphatic dicarboxylic acids, such as, for example, succinic acid, adipic acid, sebacic acid, dodecanedioic acid or cyclohexane-1,4-dicarboxylic acid.

Examples of suitable polyesters are polyethylene terephthalate, polypropylene terephthalate, polybutylene terephthalate, polyethylene 2,6-naphthalate, polypropylene 2,6-naphthalate and polybutylene 2,6-naphthalate.

The preparation of these polyesters is part of the prior art (DE-A 24 07 155 and 24 07 156; Ullmanns Encyclopädie der technischen Chemie [Ullmann's Encyclopedia of Industrial Chemistry], 4th Edn., Vol. 19, pages 65 ff., Verlag Chemie, Weinheim, 1980).

The polyester molding composition may comprise either one of these polyesters or a plurality in the form of a mixture. Furthermore, up to 40% by weight of other thermoplastics may be present so long as they do not adversely affect the bonding ability, in particular impact-modifying rubbers, as already indicated above for the polyamide. Furthermore, the polyester molding composition may comprise the conventional auxiliaries and additives for polyesters, such as, for example, flame retardants, stabilizers, processing auxiliaries, fillers, in particular for improving the electrical conductivity, reinforcing fibers, pigments or the like. The amount of said agents should be metered in such a way that the desired properties are not seriously impaired.

In general, the polyamide molding composition has a continuous polyamide phase and the polyester molding composition has a continuous polyester phase.

If the composite contains a layer of a polyamide molding composition, the adhesion promoter, in a preferred embodiment, comprises a polyamide in addition to the graft copolymer, particularly preferably from 10 to 90% by weight, based on the sum of graft copolymer and polyamide.

If the composite contains a layer of a polyester molding composition, the adhesion promoter, in a further preferred embodiment, comprises a polyester in addition to the graft copolymer, particularly preferably from 10 to 90% by weight, based on the sum of graft copolymer and polyester.

If the composite contains a layer I of a polyamide molding composition and a layer II of a polyester molding composition which are bonded to one another by the adhesion promoter according to the invention, it is preferred that the adhesion promoter comprises both a polyamide and a polyester in addition to the graft copolymer. Corresponding molding compositions are likewise a subject matter of the invention.

In this embodiment, the adhesion promoter preferably comprises the following composition:

(A) from 5 to 60 parts by weight of a graft copolymer prepared using the following momoners:

(a) from 0.5 to 25% by weight, based on the graft polymer, of a polyamine having at least 4, preferably at least 8 and particularly preferably at least 11 nitrogen atoms and having a number average molecular weight M_n of at least 146, preferably of at least 500 and particularly preferably of at least 800, and

(b) a polyamide-forming monomer selected from a lactam, an ω-aminocarboxylic acid or an equimolar combination of a diamine and a dicarboxylic acid;

(B) from 10 to 85 parts by weight of a polyamide;

(C) from 10 to 85 parts by weight of a polyester;

where the sum of the parts by weight of (A), (B) and (C) is 100; and

(D) 0 to 40 parts by weight of at least one additive selected from impact-modifying rubber and conventional auxiliaries or added materials.

The polyamide in the adhesion promoter should be readily compatible with the polyamide of layer I and thus should additionally facilitate good adhesion. Suitable polyamide combinations are known to the person skilled in the art or can easily be determined by simple routine experiments, for example by means of pressed plates. It is frequently sufficient for the two polyamides to have at least one monomer unit in common or for the two to have a monomer unit corresponding to one another with the same number of carbon atoms or with the same length. Ideally, the polyamide should substantially correspond to the polyamide of layer I.

The same applies to the polyester in the adhesion promoter, which should be readily compatible with the polyester of layer II. Here too, suitable

polyester combinations are known to the person skilled in the art or can easily be determined by simple routine experiments, for example by means of pressed plates. It is frequently sufficient for the two polyesters to have at least one monomer unit in common or for corresponding monomer units to be at least similar. Ideally, the polyester should substantially correspond to the polyester of layer II.

Besides the graft copolymer and, where appropriate, the polyamide and/or the polyester, the adhesion promoter can also comprise further components as additives, such as, for example, an impact-modifying rubber and/or auxiliaries or added materials, as explained in greater detail above as possible constituents of layers I and II. The amount of all additives is in total a maximum of 40 parts by weight, preferably a maximum of 30 parts by weight and particularly preferably a maximum of 20 parts by weight.

The multilayer composite according to the invention is, in one embodiment, a pipe, a filler neck or a tank, in particular for the transport or storage of liquids or gases. A pipe of this type can be designed in a straight or corrugated shape or is only corrugated in part sections. Corrugated pipes are prior art (for example US 5,460,771), and therefore further details in this respect are superfluous. Important applications are use as a fuel line, as a tank filler neck, as a vapor line (i.e. a line in which fuel vapors are transported, for example vent lines), as a gas station line, as a cooling fluid line, as an air-conditioning unit line or as a fuel tank.

The multilayer composite according to the invention can also be in the form of a flat composite, for example as a film, such as a packaging film for foods, as a composite element with a top layer for improving the UV resistance or as an extruded multilayer plate.

On use of the multilayer composite according to the invention for transporting or storing flammable liquids, gases or dusts, such as, for example, fuel or fuel vapors, it is advisable to provide one of the layers belonging to the composite or an additional inner layer with an electrically conductive finish. This can be carried out by compounding with an electrically conductive additive by all methods of the prior art. Examples of conductive additives which can be used are conductive black, metal flakes, metal powder, metallized glass beads, metallized glass fibers,

metal fibers (for example made from stainless steel), metallized whiskers, carbon fibers (also metallized), intrinsically conductive polymers or graphite fibrils. It is also possible to employ mixtures of different conductive additives.

In the preferred case, the electrically conductive layer is in direct contact with the medium to be transported or stored and has a maximum surface resistance of 10^9 Ω cm.

In the design of the multilayer composite according to the invention as a pipe, this can also be sheathed with an additional elastomer layer. Both crosslinking rubber compositions and thermoplastic elastomers are suitable for the sheathing. The sheathing can be applied to the pipe either with or without an additional adhesion promoter, for example by means of extrusion via a crosshead die or by pushing a prefabricated elastomer tube over the ready-extruded multilayer pipe.

The manufacture of the multilayer composite can take place in one or more steps, for example by means of one-step processes by the multi-component injection molding method, the coextrusion method or the coextrusion blow molding method, or by means of multi-step processes, as described, for example in US 5,554,425.

The multilayer composite can consist, in the simplest embodiment, of the layer I, the adhesion promoter and the layer II; if additional layers are used, however, the following layer configurations, for example, can also exist:

rubber/layer I/adhesion promoter/layer II;
layer I/adhesion promoter/layer II/electrically conductive layer II;
layer I/adhesion promoter/layer II/adhesion promoter/
layer I;
layer I/adhesion promoter/layer II/adhesion promoter/electrically conductive layer I;
rubber/layer I/adhesion promoter/layer II/adhesion promoter/layer I/electrically conductive layer I;
layer II/adhesion promoter/layer I/electrically conductive layer I.

The results given in the examples were determined with the aid of the following measurement methods.

In order to determine the carboxyl end groups, 1 g of graft copolymer was dissolved in 50 ml of benzyl alcohol at 165°C under a nitrogen blanket. The dissolution time was a maximum of 20 minutes. The solution was titrated with a solution of KOH in ethylene glycol (0.05 mol of KOH/l) against phenolphthalein until the color change.

In order to determine the amino groups, 1 g of the graft copolymer was dissolved in 50 ml of m-cresol at 25°C. The solution was titrated potentiometrically with perchloric acid.

The determination of the solution viscosity η_{rel} (relative viscosity) was carried out using a 0.5% strength by weight m-cresol solution at 25°C in accordance with DIN 53727/ISO 307.

Examples

The following components were used in the experiments:

Graft copolymer 1:

29.7 kg of laurolactam were melted at from 180°C to 210°C in a heating kettle and transferred into a pressure-tight polycondensation reactor; 1.5 kg of water and 1.71 g of hypophosphorous acid were subsequently added. The laurolactam cleavage was carried out at 280°C under the inherent pressure which became established; the mixture was then decompressed to a residual steam pressure of 3 bar over the course of 3 hours, and 300 g of polyethyleneimine (LUPASOL* G 100 from BASF AG, Ludwigshafen) were metered in. The polyethyleneimine was incorporated at the inherent pressure which became established; the mixture was subsequently decompressed to atmospheric pressure, and nitrogen was then passed over the melt at 280°C for 2 hours. The clear melt was discharged as an extrudate via a melt pump, cooled in a water bath and subsequently granulated.

η_{rel}: 1.68

Melting point T_m: 175°C

Amino group concentration: 225 mmol/kg

Carboxyl end group concentration: < 10 mmol/kg

*Trade-mark

Graft copolymer 2:
9.5 kg of laurolactam were melted at from 180°C to 210°C in a heating kettle and transferred into a pressure-tight polycondensation reactor; 475 g of water and 0.54 g of hypophosphorous acid were subsequently added. The laurolactam cleavage was carried out at 280°C under the inherent pressure which became established; the mixture was then decompressed to a residual steam pressure of 5 bar over the course of 3 hours, and 500 g of polyethyleneimine (LUPASOL* G 100 from BASF AG, Ludwigshafen) and 15 g of dodecanedioic acid were metered in. The two components were incorporated at the inherent pressure which became established; the mixture was subsequently decompressed to atmospheric pressure, and nitrogen was then passed over the melt at 280°C for 2 hours. The clear melt was discharged as an extrudate via a melt pump, cooled in a water bath and subsequently granulated.

η_{rel}: 1.52
Melting point T_m: 169°C
Amino group concentration: 810 mmol/kg
Carboxyl end group concentration: < 10 mmol/kg

PA 1: extrudable PA 12 molding composition having η_{rel} = 2.1 and an excess of carboxyl end groups

PA 2: extrudable PA 12 molding composition having η_{rel} = 2.1 and an excess of amino end groups

PES 1: VESTODUR*1000, a homopolybutylene terephthalate from Degussa-Hüls AG having a solution viscosity J, measured in phenol/o-dichlorobenzene (1:1), of 107 cm^3/g

PES 2: VESTODUR*3000, a homopolybutylene terephthalate from Degussa-Hüls AG having a solution viscosity J of 165 cm^3/g

EXXELOR*VA 1803: an EPM rubber functionalized with about 1% of maleic anhydride, from Exxon Chemical, Cologne

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Polyamide of layer I:

PA 3: Extrudable, plasticized, impact-modified PA 12 molding composition having η_{rel} = 2.1 and an excess of carboxyl end groups

Polyester of layer II:

PES 3: VESTODUR 2000, a homopolybutylene terephthalate from Degussa-Hüls AG having a solution viscosity J of 145 cm^3/g

Example 1:
A pressed-plate three-layer composite was produced from PA 3, graft copolymer 1 as adhesion promoter and PES 3 at 250°C and a pressing time of 30 seconds. Inseparable adhesion was obtained here both to the polyester layer and to the polyamide layer.

Example 2:
As Example 1, but with graft copolymer 2 as adhesion promoter. Here too, inseparable adhesion was obtained both to the polyester layer and to the polyamide layer.

Comparative Example 1:
As in Example 1, a pressed-plate composite was produced from PA 3 and PES 3. Instead of the graft copolymer 1, LUPASOL G 100 in anhydrous form was applied in a very thin layer to the upper side of the PA 3 plate which was to be bonded to PES 3.

After the pressing and cooling, the plate was removed, and the layer adhesion was tested. It was found that no adhesion was present.

Comparative Example 2:
Four different blends of PA 2 and polyethyleneimine (LUPASOL G 100 in anhydrous form, from BASF AG, Ludwigshafen) were produced in accordance with Table 1 in a Haake laboratory compounder.

Table 1: Blends of polyamide and polyethyleneimine

Blend component	Parts by weight			
PA 2	99	95	90	80
Polyethyleneimine	1	5	10	20

The mixing was carried out at 180°C and 64 rpm over the course of 8 minutes.

The mixtures were subsequently comminuted and applied to an injection-molded plate of PES 1 which was in a press mold and subsequently pressed as indicated in Example 1.

In all four cases, it was found on checking the layer adhesion that the composite could be separated at the interface even by hand.

Adhesion promoter blends:

AP 1 (not according to the invention):
12.6 kg of PA 1 and 22.82 kg of PES 1 were mixed as melts, extruded and granulated in a Berstorff*ZE 25 33D twin-screw compounder at 270°C and 200 rpm and with a throughput of 10 kg/h.

AP 2 (according to the invention):
12.6 kg of PA 2, 22.82 kg of PES 1 and 5.0 kg of graft copolymer 2 were mixed as melts, extruded and granulated in a Berstorff*ZE 25 33D twin-screw compounder at 270°C and 150 rpm and with a throughput of 10 kg/h.

AP 3 (according to the invention):
12.6 kg of PA 2, 22.82 kg of PES 2 and 5.0 kg of graft copolymer 2 were mixed as melts, extruded and granulated in a Berstorff*ZE 25 33D twin-screw compounder at 270°C and 150 rpm and with a throughput of 10 kg/h.

AP 4 (according to the invention):
As AP 3, but with additional use of 4.0 kg of EXXELOR*VA 1803.

*Trade-mark

Comparative Example 3 and Examples 3 to 5:

In order to produce the multilayer composites, a tape coextrusion mold having an exit width of 30 mm was used, with the various layers being brought together in the mold just before the exit of the melt from the mold. The mold was fed by three Storck 25 extruders. After exiting the mold, the three-layer composite was laid onto a chill roll and taken off (chill roll process).

The results are shown in the table below; the adhesion scores indicated therein have the following meanings:

0	no adhesion
1	slight adhesion
2	some adhesion; can be separated with little effort
3	good adhesion; can only be separated with great effort and possibly with the aid of tools
4	cannot be separated

Table 2: Production of three-layer tapes

Example (E) or Comparative Example (C)	Layer I	Adhesion promoter	Layer II	Adhesion	
				Layer I/adhesion promoter interface	Layer II/adhesion promoter interface
C 3	PA 3	AP 1	PES 1	0	4
E 3	PA 3	AP 2	PES 1	4	4
E 4	PA 3	AP 3	PES 3	4	4
E 5	PA 3	AP 4	PES 1	4	4

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Examples 4 and 5 according to the invention were additionally repeated in modified form by producing three-layer pipes with the corresponding layer configuration (with PA 3 as the outer layer). The results are identical (in all cases adhesion score 4).

In all the cases investigated, the long-term resistance of the multilayer composites in contact with alcohol-containing fuel was excellent both at 40°C and at 60°C.

CLAIMS:

1. A thermoplastic multilayer composite which comprises the following layers:

(I) a layer of a thermoplastic molding material;

(II) a layer of another thermoplastic molding material; and

between layer I and layer II, a layer of an adhesion promoter which comprises at least 5% by weight of a graft copolymer comprising the following monomers:

(a) from 0.5 to 25% by weight, based on the graft copolymer, of a polyamine having at least 4 nitrogen atoms and having a number average molecular weight M_n of at least 146, and

(b) a polyamide-forming monomer selected from the group consisting of a lactam, an ω-aminocarboxylic acid and an equimolar combination of a diamine and a dicarboxylic acid.

2. The thermoplastic multilayer composite as claimed in claim 1, wherein at least one of the layers (I) and (II) is made of a polyamide molding material or a polyester molding material.

3. The thermoplastic multilayer composite as claimed in claim 1 wherein the layer (I) is made of a polyamide molding material and the layer (II) is made of a polyester molding material.

4. The thermoplastic multilayer composite as claimed in claim 1, 2, or 3, wherein the polyamine contains at least 8 nitrogen atoms.

5. The thermoplastic multilayer composite as claimed in any one of claims 1 to 4, wherein the polyamine contains at least 11 nitrogen atoms.

6. The thermoplastic multilayer composite as claimed in any one of claims 1 to 5, wherein the polyamine has a number average molecular weight M_n of at least 500.

7. The thermoplastic multilayer composite as claimed in any one of claims 1 to 6, wherein the polyamine has a number average molecular weight M_n of at least 800.

8. The thermoplastic multilayer composite as claimed in any one of claims 1 to 7, wherein the graft copolymer has an amino group concentration in the range from 100 to 2500 mmol/kg.

9. The thermoplastic multilayer composite as claimed in any one of claims 1 to 8, wherein the polyamine is selected from the group consisting of:

(i) a polyvinylamine,

(ii) a polyamine prepared from an alternating polyketone,

(iii) a dendrimer that is $((H_2N-(CH_2)_3)_2N-(CH_2)_3)_2-N-(CH_2)_2-N((CH_2)_2-N((CH_2)_3-NH_2)_2)_2$, tris(2-aminoethyl)amine, N,N-bis(2-aminoethyl)-N',N'-bis[2-[bis(2-aminoethyl)amino]ethyl]-1,2-ethanediamine, or 3,15-bis(2-aminoethyl)-6,12-bis[2-[bis(2-aminoethyl)amino]ethyl]-9-[2-[bis[2-bis(2-aminoethyl)amino]ethyl]-3,6,9,12,15-pentaazaheptadecane-1,17-diamine;

(iv) a linear polyethyleneimine obtainable by polymerization of 4,5-dihydro-1,3-oxazole followed by hydrolysis, and

(v) a branched polyethyleneimine obtainable by

polymerization of aziridine and having the following amino group distribution:

25-46% of primary amino groups,

30-45% of secondary amino groups, and

16-40% of tertiary amino groups; and

the polyamine has a number average molecular weight M_n of at most 20,000.

10. The thermoplastic multilayer composite as claimed in any one of claims 1 to 9, wherein the polyamide-forming monomer (b) is ϵ-caprolactam, ϵ-aminocaproic acid, caprylolactam, ω-aminocaprylic acid, laurolactam, ω-aminododecanoic acid, ω-aminoundecanoic acid or a combination of diamine/dicarboxylic acid selected from the group consisting of hexamethylenediamine/adipic acid, hexamethylenediamine/dodecanedioic acid, octamethylenediamine/sebacic acid, decamethylenediamine/sebacic acid, decamethylenediamine/dodecanedioic acid, dodecamethylene-diamine/dodecanedioic acid and dodecamethylenediamine/2,6-naphthalenedicarboxylic acid.

11. The thermoplastic multilayer composite as claimed in any one of claims 1 to 10 wherein the graft copolymer additionally comprises the following monomer:

c) an oligocarboxylic acid, selected from the group consisting of from 0.015 to about 3 mol% of a dicarboxylic acid and from 0.01 to about 1.2 mol% of a tricarboxylic acid, in each case based on the sum of the other polyamide-forming monomers.

12. The thermoplastic multilayer composite as claimed in claim 2 or 3, wherein the adhesion promoter comprises a polyamide, a polyester, or a combination of a polyamide and a polyester, in addition to the graft copolymer.

13. The multilayer composite as claimed in any one of claims 1 to 12, which comprises more than one layer I or more than one layer II, or more than one layer I and more than one layer II.

14. The multilayer composite as claimed in any one of claims 1 to 13, wherein one of the layers has been rendered electrically conductive.

15. The multilayer composite as claimed in any one of claims 1 to 13, which further comprises an additional, electrically conductive layer adjacent to an innermost layer.

16. The multilayer composite as claimed in any one of claims 1 to 15, in the form of a pipe.

17. The multilayer composite as claimed in claim 16 which is fully or partially corrugated.

18. The multilayer composite as claimed in any one of claims 16 and 17, which further comprises a rubber layer adjacent to an outermost layer.

19. The multilayer composite as claimed in any one of claims 16 to 18, which is a fuel line, a brake fluid line, a cooling fluid line, a hydraulic fluid line, a gas station line, an air conditioning unit line, or a vapor line.

20. The multilayer composite as claimed in any one of claims 1 to 15, in the form of a hollow article.

21. The multilayer composite as claimed in any one of claims 1 to 15 and 20, in the form of a tank, or a filler neck.

22. The multilayer composite as claimed in claim 21 wherein the tank is a fuel tank, and the filler neck is a tank filler neck.

23. A multilayer composite as claimed in any one of claims 1 to 15, in the form of a film or a multilayer plate.

24. A multilayer composite as claimed in any one of claims 1 to 23, produced by multi-component injection molding, coextrusion, or coextrusion blow molding.

25. A molding composition which comprises the following components:

(A) from 5 to 60 parts by weight of a graft copolymer

comprising the following monomers:

(a) from 0.5 to 25% by weight, based on the graft copolymer, of a polyamine having at least 4 nitrogen atoms and having a number average molecular weight M_n of at least 146 and

(b) polyamide-forming monomer selected from the group consisting of a lactam, an ω-aminocarboxylic acid and an equimolar combination of a diamine and a dicarboxylic acid;

(B) from 10 to 85 parts by weight of a polyamide;

(C) from 10 to 85 parts by weight of a polyester;

where the sum of the parts by weight of (A), (B) and (C) is 100; and

(D) 0 to 40 parts by weight of at least one additive selected from the group consisting of impact-modifying rubber, and auxiliaries.

26. The molding composition according to claim 25, wherein the polyamine is

(i) a polyvinylamine,

(ii) a polyamine prepared from an alternating polyketone,

(iii) a dendrimer that is $((H_2N-(CH_2)_3)_2N-(CH_2)_3)_2-N-(CH_2)_2-N((CH_2)_2-N((CH_2)_3-NH_2)_2)_2$, tris(2-aminoethyl)amine, N,N-bis(2-aminoethyl)-N′,N′-bis[2-[bis(2-aminoethyl)amino]ethyl]-1,2-ethanediamine, or 3,15-bis(2-aminoethyl)-6,12-bis[2-[bis(2-aminoethyl)amino]ethyl]-9-[2-[bis[2-bis(2-aminoethyl)amino]ethyl]-3,6,9,12,15-pentaazaheptadecane-1,17-diamine;

(iv) a linear polyethyleneimine obtainable by polymerization of 4,5-dihydro-1,3-oxazole followed by hydrolysis, and

(v) a branched polyethyleneimine obtainable by polymerization of aziridine and having the following amino group distribution:

25-46% of primary amino groups,

30-45% of secondary amino groups, and

16-40% of tertiary amino groups; and

the polyamine has a number average molecular weight M_n of at most 20,000.

27. The molding composition according to claim 26, wherein the polyamine is the branched polyethyleneimine (v).

28. The molding composition according to any one of claims 25 to 27, wherein the polyamide-forming monomer (b) ε-caprolactam is ε-aminocaproic acid, caprylolactam, ω-aminocaprylic acid, laurolactam, ω-aminododecanoic acid, ω-aminoundecanoic acid or a combination of diamine/dicarboxylic acid selected from the group consisting of hexamethylenediamine/adipic acid,

hexamethylenediamine/dodecanedioic acid, octamethylenediamine/sebacic acid, decamethylenediamine/sebacic acid, decamethylenediamine/dodecanedioic acid, dodecamethylene-diamine/dodecanedioic acid and dodecamethylenediamine/2,6-naphthalenedicarboxylic acid.

29. The molding composition according to any one of claims 25 to 28, wherein the graft copolymer additionally comprises the following monomer:

c) an oligocarboxylic acid, selected from the group consisting of from 0.015 to about 3 mol% of a dicarboxylic acid and from 0.01 to about 1.2 mol% of a tricarboxylic acid, in each case based on the sum of the other polyamide-forming monomers.

30. The molding composition according to any one of claims 25 to 29, wherein the auxiliaries are selected from flame retardants, stabilizers, processing auxiliaries, fillers, reinforcing fibers, pigments and plasticizers.

31. A thermoplastic multilayer composite, which comprises:

(I) a layer of polyamide molding material,

(II) a layer of a polyester molding material, and

a layer of an adhesion promoter between the layers (I) and (II), the adhesion promoter layer being made of the molding composition as defined in any one of claims 25 to 30.

32. A thermoplastic multilayer composite according to claim 31, wherein the polyamide of the layer (I) and the polyamide (B) in the adhesion promoter have at least one monomer unit in common or have monomer units corresponding to

one another with the same carbon atom number or the same length.

33. A thermoplastic multilayer composite according to claim 31 or 32 wherein the polyester of the layer (II) and the polyester (C) in the adhesion promoter have at least one monomer unit in common or have monomer units corresponding to one another with the same carbon atom number or the same length.

34. A thermoplastic multilayer composite according to any one of claims 31 to 33, which is in the form of a pipe, a filler neck, or a tank.

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PATENT AGENTS