

MULTIPHASE THERMOPLASTIC RESIN COMPOSITIONS

The invention relates to multiphase thermoplastic resin compositions and more particularly to compositions in the form of a matrix in which encapsulated nodules are dispersed.

Many thermoplastics have to be modified by incorporating rubbers or other polymers, for example in order to modify the flexural modulus thereof or to improve the impact strength.

The Applicant has discovered that encapsulated nodules could be smaller than modules formed only from the polymer of the capsule.

This has many advantages, for example when the polymer of the matrix is transparent or even translucent, the reduction in the size of the nodules increases the transparency or makes the polymer more translucent for a constant level of dispersed phase.

US 5,070,145 describes compositions consisting of 80 parts of nylon-6 (PA-6) or nylon-6,6 (PA-6,6) in which 20 parts of a mixture (i) of a copolymer of ethylene and of an ethyl or butyl acrylate and (ii) of a copolymer of ethylene, ethyl acrylate and maleic anhydride have been dispersed. These compositions have good impact strength.

EP 284,379 describes multiphase compositions consisting of a polyamide and of an ethylene copolymer in the form of a polyamide matrix in which nodules (1) of an ethylene-ethyl acrylate-maleic anhydride copolymer are dispersed, and dispersed in these nodules (1) are nodules of polyamides. These nodules (1) are firstly prepared by dispersing a polyamide in the ethylene copolymer, and then these nodules are crosslinked and then dispersed in a polyamide. These compositions are also presented as having a good impact strength.

Patent FR 2,719,849 describes thermoplastic compositions consisting of a matrix of a thermoplastic polymer in which nodules of a second thermoplastic polymer, partially or totally encapsulated by an ethylene copolymer, are dispersed. These compositions are prepared by firstly encapsulating the second polymer and then the other polymer forming the matrix is added under conditions such that the capsules are not destroyed. This preparation is carried out in two steps which are completely separate or with one step following the other in the same extruder. These compositions have both good flexibility and good impact strength. The examples show PA-6, PA-12 or PBT (polybutylene terephthalate) matrices in which are dispersed nodules of PA-6,6 encapsulated by an ethylene-ethyl acrylate-glycidyl methacrylate copolymer. A comparative example shows that in a PA-6 matrix the PA-6,6 nodules encapsulated by the ethylene copolymer are coarser than the nodules formed only from the ethylene copolymer.

The present invention is therefore a thermoplastic composition comprising at least one polymer (M) forming a matrix in which are dispersed nodules of at least one polymer (K) which are encapsulated in at least one polymer (S) in such a way that these encapsulated nodules are smaller than the nodules of the polymer (S) which are dispersed in the matrix (M).

The polymer (M) may be a mixture of several miscible polymers forming a homogeneous phase. The same applies to the polymer (K) and the polymer (S). The compositions of the invention may also comprise several types of encapsulated nodules, for example nodules of (K1) which are encapsulated in (S) and nodules of (K2) which are encapsulated in (S) or else nodules of (K1) which are encapsulated in (S1) and nodules of (K2) which are encapsulated in (S2).

According to one particular embodiment, the present invention is a thermoplastic composition comprising at least one polymer (M) forming a matrix in which are dispersed nodules of at least one polymer (K) which are encapsulated in at least one polymer (S) such that (i) these encapsulated nodules are smaller than the nodules of the polymer (S) which are dispersed in the matrix (M) and such that (ii) the proportion of (M) in the (M) + (S) mixtures is essentially the same as the proportion of (M) in the (M) + (S) + (K) mixtures.

Thus, for example, it has been discovered that the nodules of an ethylene/alkyl acrylate/maleic anhydride copolymer in a nylon-11 (PA-11) matrix have a size of 0.2 μm while, in the same matrix, the nodules of nylon-12 (PA-12) which are encapsulated in the same ethylene/alkyl acrylate/maleic anhydride copolymer have a size of 0.07 μm (this is the size D_v (volume diameter) of the nodule together with the capsule, i.e. approximately the external diameter of the capsule).

The compositions of the invention have many advantages:

- they are more stable, the morphology of the dispersed phase being finer, that is to say that (M) and (S) have been made more compatible;

- they are essentially as flexible as the compositions of (M) comprising nodules containing only (S) since the polymer (K) may be screened with a sufficient thickness of capsule (S). We will return to this point later in the text;

- the finer morphologies also increase the strength of reweld lines;

- they are very easy to manufacture, simply by mixing (M), (K) and (S), for example in a short or barely plasticating extruder (standard or bottom-of-the-range extruder) or even directly in an injection

press, while in the prior art it is necessary to make them in 2 steps;

- they have good flexibility without losing mechanical properties; thus, compositions consisting of (M), (S) and (K) having the same flexural modulus as compositions consisting of (M) and (S) have a superior tensile strength. This superior strength may also be manifested by the higher burst pressure of a pipe manufactured by extrusion of the compositions of the invention;

- they have good impact strength;
- (M) need only be, relatively, the major phase in order for it to be the matrix and to avoid phase inversion. For example, it would therefore be possible to have 35 parts of (M), 32.5 parts of (S) and 32.5 parts of (K); and

- in addition to these compositions being particularly stable, they may be prepared and sold in the form of granules and used in conventional machines, and may also be recycled, for example if there is manufacturing scrap due to cutting operations.

The invention relates to the reduction in the size of the nodules of (S), whatever their initial size, when (K) is added.

The polymers (M) and (K) may be chosen from thermoplastics. (M) and (S) are chosen to be compatible. Since (S) is dispersed in the matrix of (M) in the form of nodules, (M) and (S) are deemed to be all the more compatible the smaller the nodules of (S) are. However, it is estimated that if the nodules of (S) are greater than 10 μm they are only slightly compatible, if the nodules are between 0.5 and 10 μm and preferably between 0.5 and 2 μm they are compatible, and below 0.5 μm they are very compatible.

(K) must be compatible with (S); (K) is therefore selected by preparing dispersions of (K) in (S) and by measuring the size of the nodules. This is

the general selection criterion and, from the various polymers (K) meeting this criterion another selection is made depending on the desired properties for the compositions of the invention. This other selection may
5 depend on the modulus, chemical properties, viscosity, melting temperature and reactivity.

As above, if the nodules of (K) in (S) are greater than 10 μm they are only slightly compatible, if the nodules are between 0.5 and 10 μm and preferably
10 between 0.5 and 2 μm they are compatible, and below 0.5 μm they are very compatible.

It is said that the compatibility of (K) with (S) is the same as the compatibility of (S) with (M) when the nodules of (S) in (M) have the same size as
15 the nodules of (K) in (S). It is not necessary for the compatibility of (K) with (S) to be superior to the compatibility of (S) with (M). Advantageously, the size of the nodules of (K) in (S) must not be greater than twice the size of the nodules of (S) in (M) and is
20 preferably approximately the same or smaller. This value of twice, and likewise the expression "approximately the same", is to be adapted to the size of the nodules, the measurement accuracy being in fact higher for the nodules greater than 1 or 5 μm than for
25 the smaller nodules.

It would not be outside the scope of the invention to carry out the test of compatibility of (K) with (S) by measuring nodules of (S) in (K) and then by proceeding as described above.

30 (K) must also not be too compatible with (M) in order for them to demix and for (K) to go into the capsule (S). If, then, (K) is strictly identical to (M), there will be nodules of (S) in (M). But (K) and (M) may, for example, be two different polyamides or
35 two polyamides derived from the same monomers and having different physical properties. The measurements of the compatibility of (M) with (S) and of (K) with

(S) are therefore carried out as indicated previously and it is checked whether (K) is encapsulated in (S) when (M), (K) and (S) are mixed together. Advantageously, (M) and (K) are selected from the same family of polymers, for example polyamides, saturated polyesters and other polymers, as will be described later. Thus, (M) and (K) may be two polyamides, two polyesters, etc.

It is also necessary to check the reduction in size of the nodules.

The mixing of (M), (K) and (S) is advantageously carried out by introducing (M), (K) and (S) simultaneously in a device for mixing (K) into the mixture of (M) and (S), or for mixing (M) into the mixture of (K) and (S) or for (S) into the mixture of (K) and (M). However, it would not be outside the scope of the invention to use various steps or different orders of addition, provided that the desired morphology is obtained.

In addition to the compatibility or incompatibility conditions, the melt flow index (MFI) of (M) is advantageously greater than that of (K).

By way of polymers (M), mention may be made of polyolefins, polyamides, fluoropolymers, saturated polyesters, polycarbonate, styrene resins, PMMA, thermoplastic polyurethanes (TPU), copolymers having polyamide blocks, copolymers having polyester blocks and polyether blocks, PVC, ethylene-vinyl alcohol copolymers (EVOH) and polyketones.

Polyamide (A) is understood to mean condensation products:

- of one or more amino acids, such as aminocaproic, 7-aminoheptanoic, 11-aminoundecanoic and 12-aminododecanoic acids, and of one or more lactams, such as caprolactam, oenantholactam and lauryllactam;
- of one or more salts or mixtures of diamines, such as hexamethylenediamine,

dodecamethylenediamine, *m*-xylylenediamine, bis(*p*-aminocyclohexyl)methane and trimethylhexamethylenediamine with diacids such as isophthalic, terephthalic, adipic, azelaic, suberic, sebacic and
 5 dodecanedicarboxylic acids;

- or of mixtures of some of these monomers, which results in copolyamides, for example PA-6/12 by the condensation of caprolactam and of lauryllactam.

Polymers having polyamide blocks and
 10 polyether blocks result from the copolycondensation of polyamide blocks having reactive ends with polyether blocks having reactive ends, such as, *inter alia*:

1) Polyamide blocks having diamine chain ends with polyoxyalkylene blocks having dicarboxylic chain
 15 ends;

2) polyamide blocks having dicarboxylic chain ends with polyoxyalkylene blocks having diamine chain ends, obtained by cyanoethylation and hydrogenation of aliphatic dihydroxylated alpha-omega polyoxyalkylene
 20 blocks called polyetherdiols;

3) polyamide blocks having dicarboxylic chain ends with polyetherdiols, the products obtained being, in this particular case, polyetheresteramides.

Polyamide blocks having dicarboxylic chain
 25 ends derive, for example, from the condensation of aminocarboxylic alpha-omega acids from lactams or of carboxylic diacids and diamines in the presence of a chain-limiting carboxylic diacid. Advantageously, the polyamide blocks are of nylon-12.

30 The number-average molar mass of the polyamide blocks is between 300 and 15,000 and preferably between 600 and 5000. The mass of the polyether blocks is between 100 and 6000 and preferably between 200 and 3000.

35 Polymers having polyamide blocks and polyether blocks may also include randomly distributed units. These polymers may be prepared by the

simultaneous reaction of the polyether and polyamide-block precursors.

For example, it is possible to react polyetherdiol, a lactam (or an alpha-omega amino acid) and a chain-limiting diacid in the presence of a small amount of water. A polymer is obtained having essentially polyether blocks and polyamide blocks of very variable length, but also the various reactants, having reacted in a random fashion, are distributed randomly along the polymer chain.

These polyamide-block polyether-block polymers, whether they derive from the copolycondensation of polyamide and polyether blocks prepared beforehand or from a one-step reaction, have, for example, Shore D hardnesses which may be between 20 and 75 and advantageously between 30 and 70 and an intrinsic viscosity of between 0.8 and 2.5 measured in *m*-cresol at 25°C.

Whether the polyether blocks derive from polyethylene glycol, from polyoxypropylene glycol or from polyoxytetramethylene glycol, they are either used as such and copolycondensed with polyamide blocks having carboxylic ends or they are aminated in order to be transformed into diamine polyethers and condensed with polyamide blocks having carboxylic ends. They may also be mixed with polyamide precursors and a chain limiter in order to make polyamide-block polyether-block polymers having randomly distributed units.

Polymers having polyamide and polyether blocks are described in Patents US 4,331,786, US 4,115,475, US 4,195,015, US 4,839,441, US 4,864,014, US 4,230,838 and US 4,332,920.

The polyether may, for example, be a polyethylene glycol (PEG), a polypropylene glycol (PPG) or a polytetramethylene glycol (PTMG). The latter is also called polytetrahydrofuran (PTHF).

Whether the polyether blocks are introduced into the chain of the polyamide-block polyether-block polymer in the form of diols or of diamines, they are called, for simplification, PEG blocks or PPG blocks or
5 PTMG blocks.

It would not be outside the scope of the invention if the polyether blocks contained different units, such as units derived from ethylene glycol, from propylene glycol or from tetramethylene glycol.

10 Advantageously, the polyamide-block polyether-block polymer is such that the polyamide is the major constituent by weight, that is to say that the amount of polyamide which is in the form of blocks and that which is possibly distributed randomly in the
15 chain represents 50% by weight or more of the polyamide-block polyether-block polymer. Advantageously, the amount of polyamide and the amount of polyether are in the (polyamide/polyether) ratio of from 50/50 to 80/20.

20 Preferably, the polyamide blocks and the polyether blocks of the same polymer (B) have respectively masses M_n of 1000/1000, 1300/650, 2000/1000, 2600/650 and 4000/1000.

The term polyolefin is understood to mean a
25 polymer containing olefin units such as, for example, ethylene, propylene or 1-butene units or any other alpha-olefin. By way of example, mention may be made of:

- polyethylenes such as LDPE, HDPE, LLDPE or
30 VLDPE, polypropylene, ethylene/propylene copolymers or metallocene PEs;

- copolymers of ethylene with at least one product selected from the salts or esters of unsaturated carboxylic acids, or the vinyl esters of
35 saturated carboxylic acids.

Advantageously, the polyolefin is selected from LLDPE, VLDPE, polypropylene, ethylene/vinyl

acetate copolymers or ethylene/alkyl (meth)acrylate copolymers. Advantageously, the density may be between 0.86 and 0.965 and the melt flow index (MFI) may be between 0.3 and 40.

5 By way of examples of fluorinated polymers, mention may be made of polyvinylidene fluoride (PVDF), copolymers containing vinylidene fluoride (VF₂), ethylene-tetrafluoroethylene copolymers, poly(tri-fluoroethylene), trifluoroethylene copolymers,
10 homopolymers and copolymers of hexafluoropropene and homopolymers and copolymers of chlorotrifluoroethylene. Advantageously, PVDF is used.

By EVOH is meant ethylene-vinyl alcohol copolymers. They derive from the hydrolysis of
15 ethylene/vinyl acetate copolymers, this hydrolysis possibly being incomplete and vinyl acetate units possibly remaining.

By way of example of polyesters, mention may be made of PET (polyethylene terephthalate), PBT
20 (polybutylene terephthalate) or PEN (polyethylene naphthenate).

Polyester-block polyether-block copolymers are copolymers having polyether units derived from polyetherdiols, such as polyethylene glycol (PEG),
25 polypropylene glycol (PPG) or polytetramethylene glycol (PTMG), carboxylic diacid units such as terephthalic acid and glycol units (ethanediol) or 1,4-butanediol. The linking of the polyethers and of the diacids forms the flexible segments while the linking of the glycol
30 or of the butanediol with the diacids forms the rigid segments of the copolyetherester.

Such copolyetheresters are described in Patents EP 402,883 and EP 405,227, the contents of which are incorporated in the present application.

35 By way of thermoplastic polyurethanes, mention may be made of polyether urethanes, for example those containing diisocyanate units, units derived from

polyetherdiols and units derived from ethanediol or from 1,4-butanediol.

Mention may also be made of polyester urethanes, for example those containing diisocyanate units, units derived from amorphous polyesterdiols and units derived from ethanediol or from 1,4-butanediol.

Polyketones are polymers containing substantially one mole of carbon monoxide for each mole of unsaturated monomer. This monomer may be selected from alpha-olefins having from 2 to 12 carbon atoms or their substitution derivatives. It may also be selected from styrene or its derivatives obtained by substitution with alkyls, such as methylstyrenes, ethylstyrene and isopropylstyrene.

Preferably, the polyketones are ethylene-carbon monoxide copolymers or ethylene-polypropylene-carbon monoxide copolymers.

When the polyketones are copolymers of ethylene, a second monomer and carbon monoxide, there are at least two ethylene units for one unit of the second monomer, and preferably from 10 to 100.

The polyketones may be represented by the formula: $-(-\text{CO}-\text{CH}_2-\text{CH}_2-)_x-(-\text{CO}-\text{A}-)_y-$ in which A denotes an unsaturated monomer having at least three carbon atoms, the x/y ratio being at least 2.

The units $-(-\text{CO}-\text{CH}_2-\text{CH}_2-)$ and $-(-\text{CO}-\text{A}-)$ are randomly distributed in the polyketone chain.

The number-average molar masses may be between 1000 and 200,000, advantageously between 20,000 and 90,000, measured by gel permeation chromatography). The melting temperatures may be between 175 and 300°C, usually between 200 and 270°C.

Syntheses of these polyketones are described in Patents US 4,843,144, US 4,880,903 and US 3,694,412, the contents of which are incorporated in the present application.

By way of examples of polymers (K), mention may be made of the same examples as the polymers (M).

The polymer (S) is any product which encapsulates (K) in a matrix (M) and such that the
5 nodules thus encapsulated are smaller than the nodules of (S) in (M). In the sense of the present invention, (S) is any product which is in the form of nodules in a matrix (M) and which is also in the form of nodules in a matrix (K) or which may be a matrix containing
10 nodules (K). Advantageously, (S) is a thermoplastic having affinities with (M) and with (K) and/or able to react with (M) and (K) or having affinities with (M) and able to react with (K), or vice versa.

For example, (S) may be a polyolefin chain
15 having polyamide grafted species or polyamide oligomers; thus (S) has affinities with polyolefins and polyamides.

(S) may also be an ethylene copolymer having maleic anhydride units; thus (S) has affinities with
20 polyethylenes and may react with polyamides.

By way of example of (S), mention may be made of functionalized polyolefins, grafted aliphatic polyesters, polyether-block polyamide-block polymers, optionally grafted, and copolymers of ethylene and an
25 alkyl (meth)acrylate and/or a vinyl ester of a saturated carboxylic acid.

(S) may also be a block copolymer having at least one block compatible with (M) and at least one block compatible with (K).

30 The functionalized polyolefin is a polymer containing alpha-olefin units and epoxy units or carboxylic acid units or carboxylic-acid anhydride units.

By way of example, mention may be made of the
35 polyolefins mentioned with regard to the polymers (M), or SBS, SIS, SEBS or EPDM block polymers grafted by unsaturated epoxys, such as glycidyl (meth)acrylate or

by carboxylic acids, such as (meth)acrylic acid, or by unsaturated carboxylic acid anhydrides, such as maleic anhydride.

Mention may also be made of:

5 - copolymers of ethylene, of an unsaturated epoxy and, optionally, of an unsaturated carboxylic acid ester or salt or of a vinyl ester of a saturated carboxylic acid. These are, for example, ethylene/vinyl acetate/glycidyl (meth)acrylate copolymers or
10 ethylene/alkyl (meth)acrylate/glycidyl (meth)acrylate copolymers;

 - copolymers of ethylene, of an unsaturated carboxylic acid anhydride and/or of an unsaturated carboxylic acid, possibly partly neutralized by a metal
15 (Zn) or an alkali metal (Li), and optionally of an unsaturated carboxylic acid ester or of a vinyl ester of a saturated carboxylic acid. These are, for example, ethylene/vinyl acetate/maleic anhydride copolymers or ethylene/alkyl (meth)acrylate/maleic anhydride
20 copolymers or ethylene/Zn or Li (meth)acrylate/maleic anhydride copolymers; and

 - polyethylene, polypropylene, ethylene-propylene copolymers which are grafted or copolymerized with an unsaturated carboxylic acid anhydride and then
25 condensed with a mono-aminated polyamide (or a polyamide oligomer. These products are described in EP 342,066.

Advantageously, the functionalized polyolefin is selected from ethylene/alkyl (meth)acrylate/maleic
30 anhydride copolymers, ethylene/vinyl acetate/maleic anhydride copolymers, ethylene-propylene copolymers which contain mostly propylene, these being grafted by maleic anhydride and then condensed with monoaminated nylon-6 or monoaminated oligomers of caprolactam.

35 Preferably, this is an ethylene/alkyl (meth)acrylate/maleic anhydride copolymer containing up to 40% by weight of alkyl (meth)acrylate and up to 10%

by weight of maleic anhydride. The alkyl (meth)acrylate may be selected from methyl acrylate, ethyl acrylate, n-butyl acrylate, isobutyl acrylate, 2-ethylhexyl acrylate, cyclohexyl acrylate, methyl methacrylate and
5 ethyl methacrylate.

By way of grafted aliphatic polyesters, mention may be made of polycaprolactone grafted by maleic anhydride, glycidyl methacrylate, vinyl esters or styrene. These products are described in Application
10 EP 711,791, the contents of which are incorporated in the present application.

The polyamide-block polyether-block polymers were described earlier with regard to the polymers (M). These products may be grafted by vinyl chloride or
15 alkyl acrylates. These products are described in Patent EP 365,398, the contents of which are incorporated in the present application.

The polymers (M), (K) and (S) may contain plasticizers, fillers, fire retardants, glass fibres,
20 etc.

The Applicant has also discovered that the ratio between the amounts of (S) and the amounts of (K) is important. For theoretical values, i.e. assuming that all the (K) is encapsulated, of the thickness of
25 the capsule, i.e. of (S), lying between 10 and 30% of the diameter of the encapsulated nodule, i.e. of the (S) + (K) assembly, the compositions of the invention benefit most from the combined presence of (S) and (K).

For values which are higher, and
30 advantageously higher than 40%, there is "screening", the encapsulated nodule producing the effects of a nodule of the same size consisting only of (S), i.e. as if (K) were replaced by (S). The advantage of the invention is nevertheless to have reduced the size of
35 the nodules. For example, if the polymers (M) must contain nodules of (S) in order to obtain such or such a property but these nodules are too coarse, then the

polymer (K) is added and the size of the nodules is reduced. (K) may be any polymer provided that it reduces the size of the nodules. Flexibility and impact properties are thus preserved, but, for example, there
5 is an improvement in transparency if (M) is suitable, this being in addition to the advantage of a 1-step process, already mentioned.

For smaller values of the thickness of the capsule, i.e. down to values which are just sufficient
10 for (M), (K) and (S) to be in accordance with the invention, i.e. to be such that the nodules of (K) encapsulated by (S) are smaller than the nodules of (S) alone in (M), the properties of (K) are "added" to those of (M). For example, if (M) is PA-6 and (K) is
15 PA-6,6, the temperature of bending under load (HDT) is increased.

For the aforementioned average thicknesses of (S), the compositions of the invention benefit from the effects of (S) and of (K).

20 It is also possible to be in a limiting case in which, at low strain, (S) essentially screens (K) and which, at high strain, (S) starts to no longer screen (K). (K) then starts to play a (structural) role by providing additional strength (as long as (K) has
25 been selected for having these properties, for example PA-6,6 while (M) is PA-11).

Thus, for example, the flexibility and impact-strength measurements would be fully improved as (S) (in this case, a highly flexible impact modifier)
30 fully screens (K). On the other hand, during bursting of a pipe (destructive property, and therefore the corollary of high strains), the nodule will deform in such a way (the thickness decreasing in the direction perpendicular to the strain) that (S) no longer
35 completely screens (K), and (K) then adds to the strength.

It would not be outside the scope of the invention if the capsules of (S) were not completely around (K), that is to say that the encapsulation were partial, provided that the size of the nodules is in accordance with the invention.

The invention is particularly useful in the case of thermoplastics (M) such as polyamides and saturated polyesters.

Advantageously, (M) and (K) are selected from the same family of polymers and (S) is selected from ethylene/alkyl (meth)acrylate/maleic anhydride copolymers, ethylene/vinyl acetate/maleic anhydride copolymers, ethylene/alkyl (meth)acrylate/glycidyl (meth)acrylate copolymers and ethylene/vinyl acetate/glycidyl (meth)acrylate copolymers.

Preferably, (M) and (K) are chosen to be very similar to each other in the same family of polymers, for example PA-11 and PA-12.

According to the preferred embodiments of the invention, polymers having the following properties or characteristics are respectively chosen for (M), (S) and (K):

rigid/flexible/rigid
 high T_g /low T_g /high T_g
 $T_g > 0^\circ\text{C}/T_g < 0^\circ\text{C}/T_g > 0^\circ\text{C}$ (T_g denotes the glass transition temperature).
 semi-crystalline/amorphous or pseudo-amorphous/semi-crystalline
 crystalline/amorphous or pseudo-amorphous/crystalline

Examples

The following designations are used:

PA-11: a nylon-11 having a M_w of between 45,000 and 55,000 and not containing a plasticizer;

PA-11 p.20: a nylon-11 of the PA-11 type containing $(7 \pm 2)\%$ by weight of BBSA (butylbenzene sulphonamide) as plasticizer;

PA-11 p.40: a nylon-11 of the PA-11 type containing $(12 \pm 2)\%$ by weight of BBSA.

PA-12: a nylon-12 of M_w of from 45,000 to 55,000.

5 L: an ethylene/butyl acrylate/maleic anhydride copolymer having as proportions by weight 79/18/3 and an MFI of 3 to 6, which is a random copolymer obtained by high-pressure radical catalysis.

MFI denotes the melt flow index.

10 LOTRYL: an ethylene/methyl acrylate copolymer having as proportions by weight 84/16 and an MFI of 0.3 at 190°C, 2.16 kg.

PA-12 p.20: a nylon-12 containing $(7 \pm 2)\%$ by weight of BBSA.

15 PA-12 p.40: a nylon-12 containing $(12 \pm 2)\%$ by weight of BBSA.

EPR_m denotes a maleicized EPR (ethylene propylene copolymer).

The results are given in the following table
20 (the % are by weight). The compositions indicated in the table correspond to a total of 100%, the percentage of the major component not appearing. For example: PA-11 p.20 + 6% L + 6% PA-12 means that there is 88% of PA-11 p.20 in the composition.

25 In Example 20 (PA-11 + 5% PASA) means a nylon-11 containing 95% of PA-11 and 5% of PASA.

PASA denotes a semi-aromatic polyamide obtained by the condensation of lauryllactam, BMACM [bis-(3-methyl-4-aminocyclohexyl)methane], isophthalic
30 acid and terephthalic acid, as described in EP 550,308.

In the table, the "expected flexural modulus" denotes the flexural modulus calculated from the percentages of the constituents without taking account of any synergy between the constituents or of the
35 morphology. Thus, in Example 5, a value of 600 MPa is expected because there is the same amount of PA and because 600 MPa was measured for Example 3 (the

difference in modulus of PA-11 and PA-12 has been neglected).

Ex. No.	C o m p a r a t i v e	Composition	Mechanical properties			
			Flexural modulus	Expected flex. mod.	Pipe burst (stress) at +23°C	Burst modulus *100
			ISO 178		NFR 12632	
			MPa		MPa	
		Unplasticized PA-11 family				
1	x	PA12	1100			
2	x	PA11	1000			
3	x	" + 25% L	600			
4	x	" + 50% L	320		18	6
5		" + 25% L + 25% PA12	450	600	31	7
29	x	" + 10% L	860			
		Superflexible (150-200 MPa) plasticized PA-11 family				
6	x	PA11 p40	300		24	
7	x	PA11f15	160		14	8
8'	x	PA11p40 + 25% L + 5% Lotryl	180		15	8
8	x	PA11p40 + 30% L	180		15	8
9		PA11p40 + 15% L + 15% PA12	185	255	20	11
		Flexible (300 - 350 MPa) plasticized PA-11 family				
10	x	PA11p20	420		32	
6	x	PA11p40	300		24	8
11	x	PA11p20 + 12% L	320		24	8
12		PA11p20 + 6% L + 6% PA12	340	430	29	9
		Various				
13	x	PA12p40	400		25	
14	x	PA12p40 + 30% L	195			
15		PA12p40 + 15% L + 15% PA12	225	325	21	9
16	x	PA11p20 + 5% mEPR + 7% PA12	360		28	8
12'		PA11p20 + 5% L + 7% PA12	355	450	29	8
17		PA11p40 + 10% L + 20% PA12	215		22	10
18	x	PA11p40 + 10% L + 20% HDPE	310		22	7
19	x	PA11p20 + 5% L + 7% PA6	380		29	8
20		(PA11+5%PASA) +6% L +6% PA12	1000			
		Unplasticized PA-12 family				
28	x	PA12	1100			
25	x	PA12 + 15% L	880			
26	x	PA12 + 30% L	715		27.5	3.8
27		PA12 + 15% L + 15% PA11	740	860	30.5	4.1

Table 1

REPLACEMENT SHEET (RULE 26)

Composition		Mechanical properties		Optical properties	
		Tension: stress at 50% elongation	Notched Charpy impact -40°C (new standard)	Transparency	
				Good if high	Good if low
				Transmission (560 nm, 2 mm)	Opacity
		ISO R 527	ISO 179:93		
		MPa	kJ/m ²	%	%
Unplasticized PA-11 family					
1	x PA12		7	10	35
2	x PA11		13	33	36
3	x " + 25% L		15	23	46
4	x " + 50% L		18	15	60
5	" + 25% L + 25% PA12		20	27	43
29	x " + 10% L		14	14	52
Superflexible (150-200 MPa) plasticized PA-11 family					
6	x PA11 p40		6	19	40
7	x PA11f15	15	2	28	43
8'	x PA11p40 + 25% L + 5% Lotryl	16.5	7	13	58
8	x PA11p40 + 30% L	16.5	7	14	57
9	PA11p40 + 15% L + 15% PA12	23	9	20	48
Flexible (300 - 350 MPa) plasticized PA-11 family					
10	x PA11p20		10	25	40
6	x PA11p40	24.5	6	19	40
11	x PA11p20 + 12% L	24.5	8	16	54
12	PA11p20 + 6% L + 6% PA12	31	17	21	47
Various					
13	x PA12p40		4		
14	x PA12p40 + 30% L		5	10	47
15	PA12p40 + 15% L + 15% PA12			17	40
16	x PA11p20 + 5% mEPR + 7% PA12			1	63
12'	PA11p20 + 5% L + 7% PA12			22	47
17	PA11p40 + 10% L + 20% PA12		9	20	48
18	x PA11p40 + 10% L + 20% HDPE		8	9	56
19	x PA11p20 + 5% L + 7% PA6		8	16	53
20	(PA11+5%PASA) +6% L +6% PA12			21	40
Unplasticized PA-12 family					
28	x PA12		6		
25	x PA12 + 15% L				
26	x PA12 + 30% L		9.5	mod.	mod.
27	PA12 + 15% L + 15% PA11		10	good	good

Table 1 (1st continuation)

Ex. No.	C o m p a r a t i v e	Composition	Viscosity MFI 235°C, 5kg	Manufacture (possible even on a short, low- mixing extruder)	Exudation (loss of plasticizer when hot)	Morphology	Encapsulation
						Nodule diameter D _v (SEM)	Is K encapsulated?
			g/10 min		†	µm	
		Unplasticized PA-11 family					
1	x	PA12					
2	x	PA11					
3	x	" +25% L				0.2	
4	x	" +50% L				0.3	
5		" +25% L + 25% PA12				0.2	yes
29	x	" +10% L				0.2	
		Superflexible (150 - 200 MPa) plasticized PA-11 family					
6	x	PA11p40					
7	x	PA11f15		yes	-31%		
8'	x	PA11p40 +25% L +5% Lotryl		no	-9%	0.2	
8	x	PA11p40 + 30% L		no	-9%	0.2	
9		PA11p40 + 15% L + 15% PA12		yes	-9%	0.07	yes
		Flexible (300 - 350 MPa) plasticized PA-11 family					
10	x	PA11p20					
6	x	PA11p40		yes	-13%		
11	x	PA11p20 + 12% L			-6%	0.2	
12		PA11p20 + 6% L + 6% PA12		yes	-6%	0.07	yes
		Various					
13	x	PA12p40	10				
14	x	PA12p40 + 30% L	0.3	no	-9%	0.2	
15		PA12p40 + 15% L + 15% PA	3	yes	-9%	0.07	yes
16	x	PA11p20 + 5% mEPR + 7% PA12			-6%	0.8	no
12'		PA11p20 + 5% L + 7% PA12			-6%	0.07	
17		PA11p40 + 10% L + 20% PA12		yes	-9%	0.07	yes
18	x	PA11p40 + 10% L + 20% HDPE			-9%	0.9	yes
19	x	PA11p20 + 5% L + 7% PA6			-6%	0.6	yes
20		(PA11+5%PASA) + 6% L + 6% PA12				0.07	yes
		Unplasticized PA-12 family					
28	x	PA12	30				
25	x	PA12 + 15% L	9				
26	x	PA12 + 30% L	4	no		0.25	
27		PA12 + 15% L + 15% PA11	14	yes		0.15	

Table 1 (2nd continuation)
REPLACEMENT SHEET (RULE 26)

**CLAIMS**

1. Thermoplastic composition comprising at least one polymer (M) forming a matrix in which are dispersed nodules of at least one polymer (K) which are encapsulated in at least one polymer (S) in such a way that these encapsulated nodules are smaller than the nodules of the polymer (S) which are dispersed in the matrix (M).

2. Composition according to Claim 1, in which (M) is selected from polyolefins, polyamides, fluoropolymers, saturated polyesters, polycarbonate, styrene resins, PMMA, polyurethanes (TPU), copolymers having polyamide blocks, copolymers having polyester blocks and polyether blocks, PVC, ethylene-vinyl alcohol copolymers, and polyketones.

3. Composition according to Claim 1 or 2, in which (K) is selected from the same polymers as (M).

4. Composition according to any one of the preceding claims, in which (S) is selected from functionalized polyolefins, grafted aliphatic polyesters and polyamide-block polyether-block polymers, optionally grafted.

5. Composition according to one of the preceding claims, in which (M) is PA-11, (S) is an ethylene/alkyl (meth)acrylate/maleic anhydride copolymer and (K) is PA-12.

6. Composition according to one of the preceding claims, in which the thickness of the capsule is between 10 and 30% of the diameter of the encapsulated nodule (S) + (K).

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(54) Titre: COMPOSITIONS DE RESINES THERMOPLASTIQUES MULTIPHASES

(57) Abstract

The invention features a thermoplastic composition comprising at least one matrix forming polymer (M) in which are dispersed nodules of at least one polymer (K) encapsulated in at least one polymer (S) such that these encapsulated nodules are smaller than the polymer nodules (S) dispersed in the matrix (M).

(57) Abrégé

L'invention concerne une composition thermoplastique comprenant au moins un polymère (M) formant matrice dans laquelle sont dispersés des nodules d'au moins un polymère (K) encapsulés dans au moins un polymère (S) de telle sorte que ces nodules encapsulés sont plus petits que les nodules du polymère (S) dispersés dans la matrice (M).