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(54) Title: THERMOPLASTIC COMPOSITIONS HAVING LOW GLOSS AND HIGH IMPACT STRENGTH

(57) Abstract: Thermoplastic compositions are disclosed comprising a thermoplastic resin, a first impact modifier characterized by core-shell morphology and comprising a functional shell polymer, and a second impact modifier comprising a component capable of reaction with a functional shell polymer. In addition, thermoplastic compositions are also disclosed that comprise a thermoplastic resin and a loose agglomerations of particles that have open spaces, at least 50% of the loose agglomerations comprise open spaces that measure 31 to 60 % by area of the loose agglomeration, and particles that are characterized by core-shell morphology. The inventive compositions demonstrate low gloss, high impact strength, good weatherability, and good flow properties.



WO 2017/099754 A1

**THERMOPLASTIC COMPOSITIONS HAVING LOW GLOSS AND HIGH  
IMPACT STRENGTH**

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**FIELD OF THE INVENTION**

The present invention relates in general to thermoplastic compositions, and more specifically to thermoplastic compositions having low gloss and high impact strength.

10

**BACKGROUND OF THE INVENTION**

Thermoplastic compositions are used in automotive applications, and may replace painted parts, as a color may be added to the thermoplastic resin obviating any need to provide an exterior coat of paint. Automotive interior designs must feature improved component functionality without sacrificing an elegant, luxurious appearance. Automotive original equipment manufacturers (OEMs) prefer low-gloss materials for interior applications that can stand up to years of wear and tear and environmental exposure. However, many thermoplastic compositions have a high gloss, and injection molding of polycarbonate blends produces a glossy appearance requiring surface finishes or paints to deliver low gloss surfaces.

Furthermore, many thermoplastic compositions become brittle at low temperatures, which limit their use in automotive applications where a vehicle is expected to endure both cold and hot temperatures. Finally, thermoplastic compositions often do not create a molded product that is weatherable, and after a few seasons of UV/temperature/humidity exposures, cracks appear on the surface. Such negative effects of thermoplastics have prevented their adoption by automotive OEMs. Furthermore, any use of a thermoplastic resin would require it to have good flow properties to allow it to be molded into an automotive part.

Thus, a need exists for thermoplastic compositions that have improved low temperature ductility, weatherability and flow properties, while still creating a molded article with low gloss that may be used in automotive applications.

5

### **SUMMARY OF THE INVENTION**

In one embodiment, a thermoplastic composition comprises A) a thermoplastic resin; B) an impact modifier capable of reaction with a functional shell polymer, that does not comprise a functional shell polymer;  
10 and C) an impact modifier characterized by core-shell morphology and comprising a functional shell polymer.

In another embodiment, a thermoplastic composition comprises a thermoplastic resin; and loose agglomerations of particles, wherein the loose agglomerations comprise open spaces, at least 50% of the loose  
15 agglomerations comprise open spaces that measure 31 to 60 % by area of the loose agglomeration, and wherein the loose agglomerations of particles comprise particles characterized by core-shell morphology.

In yet another embodiment, the thermoplastic resin comprises a polyester selected from the group consisting of polycarbonate,  
20 polyethylene terephthalate and polybutylene terephthalate.

In still another embodiment, the thermoplastic resin comprises about 40 to about 90 wt. % of the composition, preferably about 60 to about 80 wt. %, most preferably about 65 to about 75 wt. %.

In an embodiment not yet disclosed, the loose agglomerations  
25 comprise Component B: an impact modifier and Component C: a second impact modifier.

In another embodiment, Component B is characterized by core-shell morphology. In a different embodiment, Component B may comprise a siloxane. In still another embodiment, Component B may comprise a  
30 graft base that comprises 10 to 70 wt.%, particularly preferably from 20 to 60 wt.%, silicone rubber. In yet another embodiment, Component B comprises acrylic. In still another embodiment not yet disclosed,

Component B comprises an impact modifier capable of reaction with epoxy functionality, that does not comprise epoxy functionality.

In a different embodiment, Component B or Component C comprises a core that does not include carbon-carbon double-bonds. In another different embodiment, Component B or Component C comprises acrylate, preferably methyl methacrylate.

In still another embodiment, the functional shell polymer of Component C is epoxy functionality, and the epoxy functionality of Component C may be glycidyl (meth)acrylate.

In another embodiment not yet disclosed, Component B or Component C has a glass transition temperature of  $-40^{\circ}\text{C}$  or less, preferably  $-50^{\circ}\text{C}$  or less.

In a different embodiment, Component B or Component C comprises about 60 to about 95 wt. % core, preferably about 70 to about 80 wt. % core, as a percentage of the total weight of the impact modifier's core and shell.

In yet another embodiment, Component B is present in the composition in an amount of about 5 to about 20 wt. %, preferably about 7.5 to about 15 wt. %, while or alternatively, Component C may be present in the composition in an amount of about 1 to about 10 wt. %, preferably 2 to about 7.5 wt. %.

In a new embodiment, the thermoplastic composition further comprises Component D: a vinyl (co)polymer. In this embodiment, the vinyl (co)polymer may or may not be styrene acrylonitrile. In addition, Component D may comprise about 5 to about 20 wt. % of the thermoplastic composition.

In still another embodiment, the thermoplastic composition further comprises Component E: at least one additive selected from group consisting of: flame retardants, flame retarding synergists, anti-dripping agents, antioxidants, UV absorbers, light absorbers, fillers, reinforcing agents, additional impact modifiers, lubricants, plasticizers, optical brighteners, pigments, dyes, colorants, anti-static agents, mold-release

agents, blowing agents, and combinations of any thereof. In this embodiment, Component E may comprise about 0.02 to about 1.64 wt. % of the thermoplastic composition.

In another embodiment, Component B and Component C form  
5 loose agglomerations of particles, at least 50% of the loose agglomerations comprise open spaces that measure 31 to 60 % by area of the loose agglomeration. In a different embodiment, the loose agglomerations comprise particles having a diameter between 0.4 and 4.0 microns.

10 In still another embodiment not yet disclosed, a molded part may comprise the thermoplastic composition of any of the above embodiments. In another embodiment, a molded part may comprise a thermoplastic resin and loose agglomerations of particles, at least 50% of the loose agglomerations comprise open spaces that measure 31 to 60% by area of  
15 the loose agglomeration. In yet another embodiment, there is a process for producing a molded part comprising the thermoplastic composition disclosed above, the process comprising at least one of an injection molding, an extrusion and a blow molding process.

## 20 DETAILED DESCRIPTION OF THE INVENTION

The present invention will now be described for purposes of illustration and not limitation. Reference throughout this specification to "various non-limiting embodiments," "certain embodiments," or the like, means that a particular feature or characteristic may be included in an  
25 embodiment. Thus, use of the phrase "in various non-limiting embodiments," "in certain embodiments," or the like, in this specification does not necessarily refer to a common embodiment, and may refer to different embodiments. Further, the particular features or characteristics may be combined in any suitable manner in one or more embodiments.  
30 Thus, the particular features or characteristics illustrated or described in connection with various or certain embodiments may be combined, in whole or in part, with the features or characteristics of one or more other

embodiments without limitation. Such modifications and variations are intended to be included within the scope of the present specification.

Various non-limiting embodiments disclosed and described in this specification are directed, in part, to thermoplastic compositions comprising a thermoplastic resin, a first impact modifier and a second impact modifier. In another embodiment of the present invention, the thermoplastic composition comprises a thermoplastic resin and loose agglomerations of particles comprising a first impact modifier and a second impact modifier. The thermoplastic compositions of the present invention may further include a flow modifier, and also additives such as antioxidants, UV absorbers, light absorbers, fillers, reinforcing agents, additional impact modifiers, lubricants, plasticizers, optical brighteners, pigments, dyes, colorants, flame-retarding agents, anti-static agents, mold-release agents, blowing agents, and combinations of any thereof.

15

#### **Component A**

Component A is a thermoplastic resin, which preferably comprises a polyester, such as polycarbonate, polyethylene terephthalate, polybutylene terephthalate, or a blend of one or more polyester resins. In a preferred embodiment, the thermoplastic resin comprises polycarbonate.

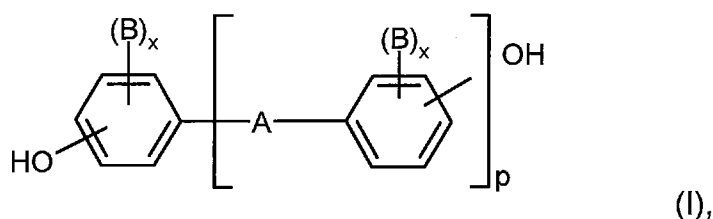
Aromatic polycarbonates and/or aromatic polyester carbonates according to component A that are suitable according to the invention are known in the literature or can be prepared by processes known in the literature (for the preparation of aromatic polycarbonates see, for example, Schnell, "Chemistry and Physics of Polycarbonates", Interscience Publishers, 1964 and DE-AS 1 495 626, DE-A 2 232 877, DE-A 2 703 376, DE-A 2 714 544, DE-A 3 000 610, DE-A 3 832 396; for the preparation of aromatic polyester carbonates see e.g. DE-A 3 077 934).

The preparation of aromatic polycarbonates can be carried out, for example, by reaction of diphenols with carbonic acid halides, preferably phosgene, and/or with aromatic dicarboxylic acid dihalides, preferably benzenedicarboxylic acid dihalides, according to the interfacial process,

optionally using chain terminators, for example monophenols, and optionally using branching agents having a functionality of three or more than three, for example triphenols or tetraphenols. Preparation by a melt polymerisation process by reaction of diphenols with, for example,

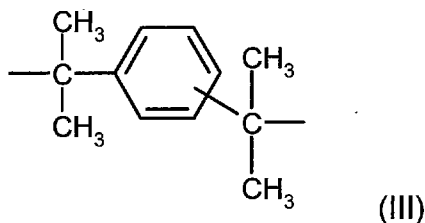
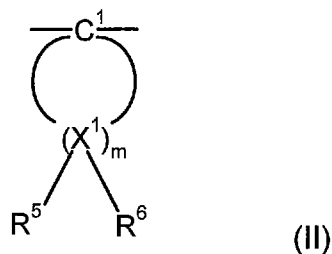
5 diphenyl carbonate is also possible.

Diphenols for the preparation of the aromatic polycarbonates and/or aromatic polyester carbonates include preferably those of formula (I)



wherein

10 A is a single bond, C<sub>1</sub>- to C<sub>5</sub>-alkylene, C<sub>2</sub>- to C<sub>5</sub>-alkylidene, C<sub>5</sub>- to C<sub>6</sub>-cycloalkylidene, O-, SO-, -CO-, -S-, -SO<sub>2</sub>-, C<sub>6</sub>- to C<sub>12</sub>-arylene, to which further aromatic rings optionally containing heteroatoms can be fused, or a radical of formula (II) or (III)



15

B is in each case C<sub>1</sub>- to C<sub>12</sub>-alkyl, preferably methyl, halogen, preferably chlorine and/or bromine,

x each independently of the other is 0, 1 or 2,

p is 1 or 0, and

$R^5$  and  $R^6$  can be chosen individually for each  $X^1$  and each independently of the other is hydrogen or C<sub>1</sub>- to C<sub>6</sub>-alkyl, preferably hydrogen, methyl or ethyl,

$X^1$  is carbon and

- 5      $m$  is an integer from 4 to 7, preferably 4 or 5, with the proviso that on at least one atom  $X^1$ ,  $R^5$  and  $R^6$  are simultaneously alkyl.

Preferred diphenols include hydroquinone, resorcinol, dihydroxydiphenols, bis-(hydroxyphenyl)-C<sub>1</sub>-C<sub>5</sub>-alkanes, bis-(hydroxyphenyl)-C<sub>5</sub>-C<sub>6</sub>-cycloalkanes, bis-(hydroxyphenyl) ethers, bis-  
 10   (hydroxyphenyl) sulfoxides, bis-(hydroxyphenyl) ketones, bis-(hydroxyphenyl)-sulfones and  $\alpha,\alpha$ -bis-(hydroxyphenyl)-diisopropyl-benzenes, and derivatives thereof brominated and/or chlorinated on the ring.

Particularly preferred diphenols include 4,4'-dihydroxydiphenyl, bisphenol A, 2,4-bis(4-hydroxyphenyl)-2-methylbutane, 1,1-bis-(4-  
 15   hydroxyphenyl)-cyclohexane, 1,1-bis-(4-hydroxyphenyl)-3,3,5-trimethylcyclohexane, 4,4'-dihydroxydiphenyl sulfide, 4,4'-dihydroxydiphenylsulfone and di- and tetra-brominated or chlorinated derivatives thereof such as, for example, 2,2-bis-(3-chloro-4-  
 20   hydroxyphenyl)-propane, 2,2-bis-(3,5-dichloro-4-hydroxyphenyl)-propane or 2,2-bis-(3,5-dibromo-4-hydroxyphenyl)-propane, 2,2-Bis-(4-hydroxyphenyl)-propane (bisphenol A) is particularly preferred.

The diphenols can be used on their own and/or in the form of arbitrary mixtures. The diphenols are known in the literature or are  
 25   obtainable according to processes known to one of skill in art in the literature.

Chain terminators suitable for the preparation of thermoplastic aromatic polycarbonates include, for example, phenol, p-chlorophenol, p-tert-butylphenol or 2,4,6-tribromophenol, but also long-chained  
 30   alkylphenols, such as 4-[2-(2,4,4-trimethylpentyl)]-phenol, 4-(1,3-tetramethylbutyl)-phenol according to DE-A 2 842 005 or monoalkylphenol or dialkylphenols having a total of from 8 to 20 carbon



atoms in the alkyl substituents, such as 3,5-di-tert-butyl-phenol, p-isooctylphenol, p-tert-octylphenol, p-dodecyl-phenol and 2-(3,5-dimethyl-heptyl)-phenol and 4-(3,5-dimethylheptyl)-phenol. The amount of chain terminators to be used is generally from 0.5 mol% to 10 mol%,

5 based on the molar sum of the diphenols used in a particular case.

The thermoplastic aromatic polycarbonates can be branched in a known manner, preferably by the incorporation of from 0.05 to 2.0 mol%, based on the sum of the diphenols used, of compounds advantageously having a functionality of three or more than three, for example those

10 having three or more phenolic groups.

Both homopolycarbonates and copolycarbonates are suitable. For the preparation of copolycarbonates of component A according to the present invention, it is also possible to use from 1 to 25 wt.%, preferably from 2.5 to 25 wt.%, based on the total amount of diphenols to be used, of

15 polydiorganosiloxanes having hydroxyaryloxy end groups. These are known (US 3 419 634) and can be prepared according to processes known in the literature. The preparation of copolycarbonates containing polydiorganosiloxanes is described in DE-A 3 334 782.

Preferred polycarbonates in addition to the bisphenol A

20 homopolycarbonates include the copolycarbonates of bisphenol A, advantageously with up to 15 mol%, based on the molar sums of diphenols, of diphenols other than those mentioned as being preferred or particularly preferred, in particular 2,2-bis(3,5-dibromo-4-hydroxyphenyl)-propane.

25 Aromatic dicarboxylic acid dihalides for the preparation of aromatic polyester carbonates can preferably be diacid dichlorides of isophthalic acid, terephthalic acid, diphenyl ether 4,4'-dicarboxylic acid and naphthalene-2,6-dicarboxylic acid.

Mixtures of the diacid dichlorides of isophthalic acid and

30 terephthalic acid in a ratio of from 1:20 to 20:1 are particularly preferred.

In the preparation of polyester carbonates, a carbonic acid halide, preferably phosgene, is additionally used concomitantly as a bifunctional acid derivative.

Suitable chain terminators for the preparation of the aromatic  
 5 polyester carbonates, in addition to the monophenols already mentioned, also include chlorocarbonic acid esters thereof and the acid chlorides of aromatic monocarboxylic acids, which can optionally be substituted by C<sub>1</sub>- to C<sub>22</sub>-alkyl groups or by halogen atoms, as well as aliphatic C<sub>2</sub>- to C<sub>22</sub>-monocarboxylic acid chlorides.

10 The amount of chain terminators is advantageously in each case from 0.1 to 10 mol%, based in the case of phenolic chain terminators on moles of diphenol and in the case of monocarboxylic acid chloride chain terminators on moles of dicarboxylic acid dichloride.

The aromatic polyester carbonates can also optionally contain  
 15 aromatic hydroxycarboxylic acids incorporated therein.

The aromatic polyester carbonates can be both linear and/or branched in any known manner (see in this connection DE-A 2 940 024 and DE-A 3 007 934).

There can optionally be used as branching agents, for example,  
 20 carboxylic acid chlorides having a functionality of three or more, such as trimesic acid trichloride, cyanuric acid trichloride, 3,3',4,4'-benzophenone-tetracarboxylic acid tetrachloride, 1,4,5,8-naphthalene-tetracarboxylic acid tetrachloride or pyromellitic acid tetrachloride, in amounts of from 0.01 to 1.0 mol% (based on dicarboxylic  
 25 acid dichlorides used), or phenols having a functionality of three or more, such as phloroglucinol, 4,6-dimethyl-2,4,6-tri-(4-hydroxyphenyl)-hept-2-ene, 4,6-dimethyl-2,4,6-tri-(4-hydroxyphenyl)-heptane, 1,3,5-tri-(4-hydroxyphenyl)-benzene, 1,1,1-tri-(4-hydroxyphenyl)-ethane, tri-(4-hydroxyphenyl)-phenylmethane, 2,2-bis[4,4-bis(4-hydroxyphenyl)-  
 30 cyclohexyl]-propane, 2,4-bis(4-hydroxyphenyl-isopropyl)-phenol, tetra-(4-hydroxyphenyl)-methane, 2,6-bis(2-hydroxy-5-methyl-benzyl)-4-methylphenol, 2-(4-hydroxyphenyl)-2-(2,4-dihydroxyphenyl)-propane, tetra-(4-

hydroxy-phenyl-isopropyl]-phenoxy)-methane, 1,4-bis[4,4'-  
dihydroxytriphenyl]-methyl]-benzene, in amounts of from 0.01 to 1.0 mol%,  
based on diphenols used. Phenolic branching agents can be placed in a  
vessel with the diphenols; acid chloride branching agents can be  
5 introduced together with the acid dichlorides if desired for any reason.

The content of carbonate structural units in the thermoplastic  
aromatic polyester carbonates can vary as desired. The content of  
carbonate groups is preferably up to 100 mol%, in particular up to 80  
mol%, particularly preferably up to 50 mol%, based on the sum of ester  
10 groups and carbonate groups. Both the esters and the carbonates  
contained in the aromatic polyester carbonates can be present in the  
polycondensation product in the form of blocks and/or distributed  
randomly.

In a preferred embodiment of the present invention, the aromatic  
15 polycarbonates and aromatic polyester carbonates advantageously have a  
weight-average molecular weight ( $M_w$ , measured, for example, by GPC,  
based on polystyrene standards using a Universal Calibration Method  
reporting polycarbonate numbers. A Waters Alliance Gel Permeation  
Chromatograph is used to perform the separation. The data analysis is  
20 done using EmpowerPro3 software. The chromatographic conditions are:  
temperature: 35C in columns & detector; solvent is tetrahydrofuran (THF);  
flow rate is 1.0 ml/min.; flow standard is toluene; injection volume is 75 $\mu$ l;  
operating pressure is 760 psi; sample concentration is 0.5%) of from  
22,000 to 32,000 g/mol, particularly preferably from 24,000 to 28,000  
25 g/mol.

The thermoplastic aromatic polycarbonates and polyester  
carbonates can be used on their own and/or in an arbitrary mixture.

In various non-limiting embodiments, commercially-available  
polycarbonate resins may be used in polycarbonate compositions. Non-  
30 limiting examples of suitable polycarbonate resins include, for example,  
the bisphenol-based polycarbonate resins available from Covestro under  
the MAKROLON trade name. Additional polycarbonate resins that may be

used in various non-limiting embodiments are described, for example, in U.S. Pat. Nos. 3,030,331; 3,169,121; 3,395,119; 3,729,447; 4,255,556; 4,260,731; 4,369,303; 4,714,746; 5,693,697, which are all incorporated by reference herein, and in U.S. Patent Application Publication Nos.

5 2007/0123634; 2008/0132617; 2010/0160508; and 2011/0003918, which are also incorporated by reference herein.

Component A may comprise about 40.0 wt.% to about 90.0 wt.% of the thermoplastic composition, preferably about 60.0 wt.% to about 80.0 wt.% of the composition, most preferably, about 65.0 wt.% to about 75.0  
10 wt.%, wherein the wt.%, all instances, is based on total composition weight.

### **Component B**

Component B is an impact modifier, characterized by graft  
15 copolymer B. Graft copolymer B can generally be prepared by radical polymerization, for example by emulsion, suspension, solution or mass polymerization, preferably by emulsion polymerization. Component B comprises monomer B.1 and optionally graft base B.2.

Suitable monomers B.1 include vinyl monomers such as vinyl  
20 aromatic compounds and/or vinyl aromatic compounds substituted on the ring (such as styrene,  $\alpha$ -methylstyrene, p-methylstyrene, p-chlorostyrene), methacrylic acid (C<sub>1</sub>-C<sub>8</sub>)-alkyl esters (such as methyl methacrylate, ethyl methacrylate, 2-ethylhexyl methacrylate, allyl methacrylate), acrylic acid (C<sub>1</sub>-C<sub>8</sub>)-alkyl esters (such as methyl acrylate, ethyl acrylate, n-butyl  
25 acrylate, tert-butyl acrylate), organic acids (such as acrylic acid, methacrylic acid) and/or vinyl cyanides (such as acrylonitrile and methacrylonitrile) and/or derivatives (such as anhydrides and imides) of unsaturated carboxylic acids (for example maleic anhydride and N-phenyl-maleimide). These vinyl monomers can be used on their own or in  
30 mixtures of at least two monomers.

Preferred monomers B.1 can be selected from at least one of the monomers styrene, methyl methacrylate, n-butyl acrylate and acrylonitrile. Particular preference is given to the use of methyl methacrylate or a mixture of styrene and acrylonitrile as the monomer B.1.

5           Component B may optionally include graft base B.2. The glass transition temperature of the graft base B.2 is typically  $< 10^{\circ}\text{C}$ , preferably  $< 0^{\circ}\text{C}$ , particularly preferably  $< -20^{\circ}\text{C}$ . The graft base B.2 generally has a mean particle size ( $d_{50}$  value) of from 0.05 to 10  $\mu\text{m}$ , preferably from 0.06 to 5  $\mu\text{m}$ , particularly preferably from 0.1 to 1  $\mu\text{m}$ .

10           The mean particle size ( $d_{50}$  value) is the diameter above and below which in each case 50 wt.% of the particles lie. It can be determined by means of ultracentrifuge measurement (W. Scholtan, H. Lange, Kolloid-Z. und Z. Polymere 250 (1972), 782-796).

            The graft base B.2 can comprise composite rubbers of silicone  
15   rubber and acrylate rubber, these two types of rubber being present, for example, in the form of a physical mixture or the silicone rubber and the acrylate rubber, for example, forming an interpenetrating network as a result of their preparation or, for example, the silicone rubber and the acrylate rubber forming a graft base that has a core-shell structure.

20   Preferred graft bases B.2 include composite rubbers of from 10 to 70 wt.%, particularly preferably from 20 to 60 wt.%, silicone rubber and from 90 to 30 wt.%, particularly preferably from 80 to 40 wt.%, butyl acrylate rubber (the indicated wt.% is here based in each case on the graft base B.2). In comparison to "pure" acrylate rubber based impact modifiers,  
25   impact modifiers that include a silicon component offer the potential to further optimize low temperature ductility of the resulting blends. Notably, the glass transition temperature of the silicone rubber portion is significantly lower than that of acrylate rubbers. For example, the glass transition temperature for dimethylsiloxane rubber is  $-112^{\circ}\text{C}$ , compared  
30   with  $-40$  to  $-60^{\circ}\text{C}$  for acrylate rubbers.

The silicone-acrylate rubbers are preferably composite rubbers having at least one graft-active site. The silicone rubber and the acrylate rubber preferably interpenetrate in the composite rubber so that they cannot substantially be separated from one another.

5       Silicone-acrylate rubbers are known and described, for example, in US 5,807,914, EP 430134 and US 4888388.

      Silicone rubber components of the silicone-acrylate rubber according to B.2 can preferably be prepared by emulsion polymerization, in which the siloxane monomer structural units, crosslinkers or branching  
10       agents (IV) and optionally grafting agents (V) can be used.

      There can be used as the siloxane monomer structural units, for example and preferably, dimethylsiloxane or cyclic organosiloxanes having at least 3 ring members, preferably from 3 to 6 ring members, such as, for example and preferably, hexamethylcyclotrisiloxane, octamethyl-  
15       cyclotetrasiloxane, decamethylcyclopentasiloxane, dodecamethyl-  
      cyclohexasiloxane, trimethyl-triphenyl-cyclotrisiloxane, tetramethyl-  
      tetraphenyl-cyclotetrasiloxane, octaphenylcyclotetrasiloxane.

      The organosiloxane monomers can be used on their own and/or in the form of mixtures of 2 or more monomers. The silicone rubber  
20       preferably contains not less than 50 wt.% and particularly preferably not less than 60 wt.% organosiloxane, based on the total weight of the silicone rubber component.

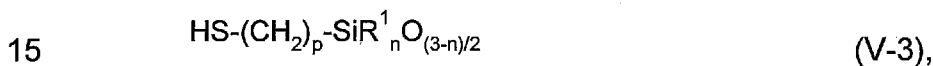
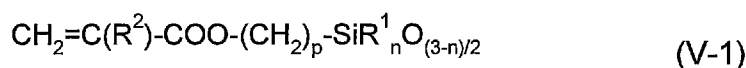
      As crosslinkers or branching agents (IV) there can be preferably used silane-based crosslinkers having a functionality of 3 or 4, particularly  
25       preferably 4. Preferred examples which may be mentioned include: trimethoxymethylsilane, triethoxyphenylsilane, tetramethoxysilane, tetraethoxysilane, tetra-n-propoxysilane and tetrabutoxysilane. The crosslinker can be used on its own and/or in a mixture of two or more. Tetraethoxysilane is particularly preferred in some cases.

30       A crosslinker can be used, for example, in an amount in the range from 0.1 to 40 wt.%, based on the total weight of the silicone rubber component. The amount of crosslinker is preferably so chosen that the

degree of swelling of the silicone rubber, measured in toluene, is from 3 to 30, preferably from 3 to 25 and particularly preferably from 3 to 15. The degree of swelling is defined as the weight ratio of the amount of toluene absorbed by the silicone rubber when it is saturated with toluene at 25°C and the amount of silicone rubber in the dry state. The determination of the degree of swelling is described in detail in EP 249964, which is incorporated herein by reference.

Tetrafunctional branching agents are often preferred to trifunctional branching agents because the degree of swelling can then more easily be controlled within the above-described limits.

Suitable grafting agents (V) are compounds that are capable of forming structures of the following formulae:



wherein

$\text{R}^1$  represents  $\text{C}_1$ - $\text{C}_4$ -alkyl, preferably methyl, ethyl or propyl, or phenyl,

$\text{R}^2$  represents hydrogen or methyl,

$n$  denotes 0, 1 or 2 and

$p$  denotes an integer from 1 to 6.

Acryloyl- or methacryloyl-oxysilanes are particularly suitable for forming the above-mentioned structure (V-1) and have a high grafting efficiency. Effective formation of the graft chains is thereby often ensured, and the impact strength of the resulting resin composition is accordingly typically promoted. Preferred examples which may be mentioned include:  $\beta$ -methacryloyloxy-ethyldimethoxymethyl-silane,  $\gamma$ -methacryloyloxy-propylmethoxydimethyl-silane,  $\gamma$ -methacryloyloxy-propyldimethoxy-methyl-silane,  $\gamma$ -methacryloyloxy-propyltrimethoxy-silane,  $\gamma$ -methacryloyloxy-propylethoxy-diethyl-silane,  $\gamma$ -methacryloyloxy-propyldiethoxymethyl-silane,  $\delta$ -methacryloyl-oxy-butyldiethoxymethyl-silane or mixtures thereof.

Preferably from 0 to 20 wt.% of a suitable grafting agent, based on the total weight of the silicone rubber, is used.

The silicone rubber can be prepared by any method such as emulsion polymerization, as described, for example, in US 2891920 and  
5 US 3294725. The silicone rubber is thereby obtained in the form of an aqueous latex. To that end, a mixture containing organosiloxane, crosslinker and optionally grafting agent is mixed with water, with shearing, for example by means of a homogenizer, in the presence of an emulsifier based, in a preferred embodiment, on sulfonic acid, such as, for example,  
10 alkylbenzenesulfonic acid or alkylsulfonic acid, the mixture polymerizing completely to give the silicone rubber latex. An alkylbenzenesulfonic acid is particularly suitable because it acts not only as an emulsifier but also as a polymerization initiator. In this case, a combination of the sulfonic acid with a metal salt of an alkylbenzenesulfonic acid or with a metal salt of an  
15 alkylsulfonic acid is advantageous because the polymer is thereby stabilized during the subsequent graft polymerization.

After the polymerization, the reaction is ended by neutralizing the reaction mixture by adding an aqueous alkaline solution, for example by adding an aqueous sodium hydroxide, potassium hydroxide or sodium  
20 carbonate solution.

Suitable polyalkyl (meth)acrylate rubber components of the silicone-acrylate rubbers according to B.2 can be prepared, for example, from methacrylic acid alkyl esters and/or acrylic acid alkyl esters, a crosslinker (VI) and a grafting agent (VII). Examples of preferred methacrylic acid alkyl  
25 esters and/or acrylic acid alkyl esters include the C<sub>1</sub>- to C<sub>8</sub>-alkyl esters, for example methyl, ethyl, n-butyl, tert-butyl, n-propyl, n-hexyl, n-octyl, n-lauryl and 2-ethylhexyl esters; haloalkyl esters, preferably halo-C<sub>1</sub>-C<sub>8</sub>-alkyl esters, such as chloroethyl acrylate, and mixtures of these monomers. n-Butyl acrylate is particularly preferred.

30



Preferable rubber graft bases B.2 are ones without carbon-carbon double bonds, such as those present in –diene compounds, like ABS. Carbon-carbon double bonds are less stable than carbon-carbon single bonds, and can become unstable through exposure to sunlight. Thus, preferable graft bases B.2 do not contain carbon-carbon double bonds.

As crosslinkers (VI) for the polyalkyl (meth)acrylate rubber component of the silicone-acrylate rubber there can be used monomers having more than one polymerizable double bond. Preferred examples of crosslinking monomers include esters of unsaturated monocarboxylic acids having from 3 to 8 carbon atoms and unsaturated monohydric alcohols having from 3 to 12 carbon atoms, or saturated polyols having from 2 to 4 OH groups and from 2 to 20 carbon atoms, such as ethylene glycol dimethacrylate, propylene glycol dimethacrylate, 1,3-butylene glycol dimethacrylate and 1,4-butylene glycol dimethacrylate. The crosslinkers can be used on their own or in mixtures of at least two crosslinkers.

Examples of preferred grafting agents (VII) include allyl methacrylate, triallyl cyanurate, triallyl isocyanurate or mixtures thereof. Allyl methacrylate can also be used as crosslinker (VI). The grafting agents can be used on their own and/or in mixtures of at least two grafting agents.

The amount of crosslinker (VI) and grafting agent (VII) is advantageously from 0.1 to 20 wt.%, based on the total weight of the polyalkyl (meth)acrylate rubber component of the silicone-acrylate rubber.

The silicone-acrylate rubber can be prepared, for example, by first preparing the silicone rubber according to B.2.1 in the form of an aqueous latex. The latex is then enriched with the methacrylic acid alkyl esters and/or acrylic acid alkyl esters that are to be used, the crosslinker (VI) and the grafting agent (VII), and a polymerization is carried out. Preference is given to an emulsion polymerization initiated by radicals, for example by a peroxide, an azo or a redox initiator. Particular preference is given to the use of a redox initiator system, especially of a sulfoxylate initiator system

prepared by combination of iron sulfate, disodium ethylenediaminetetraacetate, rongalite and hydroperoxide.

The grafting agent (V) that is used in the preparation of the silicone rubber preferably has the effect of bonding the polyalkyl (meth)acrylate rubber component covalently to the silicone rubber component. In the polymerization, the two rubber components interpenetrate and thus form the composite rubber, which can no longer be separated into its constituents of silicone rubber component and polyalkyl (meth)acrylate rubber component after the polymerization.

For the preparation of the silicone-acrylate graft polymers B mentioned as component B, the monomers B.1 can be grafted on to the rubber base B.2.

The polymerization methods described, for example, in EP 249964, EP 430134 and US 4888388 can be used thereby.

For example, the graft polymerization can advantageously be carried out according to the following polymerization method: In a single- or multi-stage emulsion polymerization initiated by radicals, the desired vinyl monomers B.1 are polymerized on to the graft base, which is present in the form of an aqueous latex. The grafting efficiency should thereby be as high as possible and is preferably greater than or equal to 10%. The grafting efficiency is significantly dependent on the grafting agent (V) or (VII) that is used. After the polymerization to the silicone (acrylate) graft rubber, the aqueous latex is added to hot water, in which metal salts, such as, for example, calcium chloride or magnesium sulfate, have previously been dissolved. The silicone (acrylate) graft rubber thereby coagulates and can subsequently be separated.

In an embodiment where Component B comprises core-shell morphology, Component B comprises about 60 to about 95 wt. % core, preferably 70 to about 90 wt. % core B.2, with the remaining amount in Component B being the shell B.1. The glass transition temperature of Component B is preferably -40°C or less, most preferably -50°C or less.

Component B may be, but is not limited to, impact modifiers having a core-shell morphology as disclosed above. Preferably, Component B does not comprise a functional shell polymer. Component B may comprise about 5 wt.% to about 20 wt.% of the thermoplastic composition, preferably about 7.5 wt.% to about 15 wt.% of the composition, wherein the wt.%, all instances, is based on total composition weight.

### **Component C**

Component C is also an impact modifier, and is also characterized by graft copolymer B hereinabove. However, component C differs from component B, in that it comprises core-shell morphology and a functional shell polymer in its shell corresponding to shell B.1 described above.

In addition to the monomers described in B.1 above, the shell of component C also includes a functional shell polymer. By "functional shell polymer", as used herein, means either a blend of functional and non-functional polymers, or at least one copolymer containing one or more different functional groups, either in the copolymer backbone, as pendant groups, or both. The functionalized copolymer may be formed in several different ways, as known in the art. These include copolymerization (random or block) of one or more functional monomers with non-functional monomers, grafting, and post-polymerization functionalization of a polymer, or a mixture thereof.

Non-functional ethylenically unsaturated monomers useful in forming the shell polymer include, but are not limited to, styrene, (meth)acrylonitrile, ethyl acrylate, propyl acrylate, butyl acrylate, methyl methacrylate, divinyl benzene, acrylonitrile, and mixtures thereof.

Functional monomers useful as comonomers to add functionality to the copolymer include, but are not limited to, those containing acid, anhydride, hydroxy, epoxy, and amine groups. Examples of useful functional comonomers include, but are not limited to: N,N-dimethylaminoethyl(meth)acrylate, N,N-diethylaminoethyl (meth)acrylate, (meth)acrylamide, N,N-dimethylacrylamide, N-methylolacrylamide, N-

methylaminopropyl(meth)acrylamide, N,N-dimethylaminopropyl(meth)acrylamide, N-ethylamino propyl(meth)acrylamide, N,N-diethylaminopropyl (meth)acrylamide, N-methylacrylamide or N-t-butylacrylamide or N-ethyl (meth)acrylamide or chlorides of these compounds, 2-hydroxyethyl(meth)acrylate, hydroxypropyl(meth)acrylate, 4-hydroxybutyl (meth)acrylate, glycidyl(meth)acrylate, ethyl alpha-hydroxymethacrylate, and 2,3-dihydroxypropyl(meth)acrylate, maleic anhydride, maleic acid, substituted maleic anhydride, mono-ester of maleic anhydride, itaconic anhydride, itaconic acid, substituted itaconic anhydride, glutaric anhydride, monoester of itaconic acid, fumaric acid, fumaric anhydride, fumaric acid, substituted fumaric anhydride, monoester of fumaric acid, crotonic acid and its derivatives, acrylic acid, and methacrylic acid; cyanoalkoxyalkyl (meth)acrylates such as omega-cyanoethoxyethyl acrylate, or omega-cyanoethoxyethyl methacrylate; vinyl monomers containing an aromatic ring and an hydroxyl group, such as vinylphenol, para-vinylbenzyl alcohol, meta-vinylphenethyl alcohol, vinyl pyrrolidone, and vinyl imidazole; and other functional monomers, allyl cellosolve, allyl carbinol, methylvinyl carbinol, allyl alcohol, methyllyl alcohol, glycidyl methacrylate, 3,4-epoxybutyl acrylate, acrylonitrile, methacrylonitrile, beta-cyanoethyl methacrylate, beta-cyanoethyl acrylate, Examples of polymerizable surfactants or macromonomers with hydrophilic moieties useful in the present invention include, but are not limited to sodium 1-allyloxy-2-hydroxypropane sulfonate, phosphate methacrylate monomer, poly(ethylene glycol)methylether methacrylate, 1-methacrylamido, 2-imidazolidinone ethane. A preferred functionality of Component C is epoxy functionality.

Epoxy monomers, or resins, contain a reactive oxirane structure which is commonly referred to as an "epoxy functionality." The most popular epoxy monomers are those derived from the reaction of bis(4-hydroxy phenylene) - 2,2 propane (called bisphenol A) and 1-chloroprene 2-oxide (called epichlorohydrin), in the presence of sodium hydroxide. The

structure of the major product, bisphenol A diglycidyl ether (DGEBA or BADGE) and its condensed forms, is dependent upon the stoichiometry of the reactants. Typical monomers ("resins") are marketed with  $n$  values lying in the range 0.03 – 10. At room temperature these monomers are  
5 crystalline solids for  $n$  values close to zero, liquids for  $n$  values up to  $n = 0.5$ , and amorphous solids (glass transition temperature,  $T_g \sim 40 - 90^\circ \text{C}$ ) for higher  $n$  values.

Another major group of epoxy monomers derived from epichlorohydrin is that comprising monomers synthesized with an aromatic  
10 amine, such as methylene dianiline (TGMDA). Oxirane groups can be generated by peroxidation of carbon – carbon double bonds. Types of such oligomers are epoxidized oils or cycloaliphatic oxides. Epoxy monomers containing vinyl groups, like glycidyl (meth)acrylate or glycidyl oxystyrene, can be used for the synthesis of functional oligomers. Linear  
15 or crosslinked epoxy polymers are obtained by reaction of the epoxy monomers with co - monomers ("hardeners") and/or initiators. Epoxy polymers can be produced by step or chain polymerizations or, eventually, by a combination of both mechanisms. Step - growth polymerization proceeds via a step - by - step succession of elementary reactions  
20 between reactive sites. Each independent step causes the disappearance of two co - reacting sites and creates a new covalent bond between a pair of functional groups. The number of reactive sites per monomer (functionality) and the molar ratio between co - reactive sites are the main parameters that control the polymer structure.

25 To obtain linear polymers, the reactants must be bifunctional; monofunctional reactants interrupt the polymer growth. A condition to obtain crosslinked polymers is that at least one of the monomers has a functionality higher than 2. The molar mass of the product grows gradually and the polydispersity tends to 2 for a linear polymer; for a crosslinked  
30 polymer the mass – average molar mass becomes infinite at a critical conversion (gelation).

Chain - growth polymerization is characterized by the presence of initiation, propagation, chain transfer and termination steps. In the case of epoxies, the initiation step produces an ion (either an anion or a cation) that is called the active center of the polymerization. The ion may be  
5 generated by a chemical reaction or by an adequate source of irradiation. Once active centers are generated they produce primary chains by the consecutive addition of monomers through the propagation step of the reaction. As active centers are always present at the end of primary chains, the propagation reaction continues until it becomes interrupted by  
10 a chain transfer step or a termination step. The main parameters controlling the polymer structure are the functionality of monomers, the molar ratio between initiator and monomers, the concentration of species that are involved in chain transfer steps, and temperature (thermal cycle) that affects the relative rates of different steps.

15 In a preferred embodiment, the epoxy functionality of component C is glycidyl (meth)acrylate, or GMA. The GMA monomer can react with an extremely wide range of monomers and functionalized molecules, providing greater flexibility and freedom in polymer design, as well as performance benefits in the resulting thermoplastic formulation. GMA  
20 functional polymers comprise at least one unit derived from glycidyl ester monomer(s). The glycidyl ester polymer may be a polymer, copolymer, or terpolymer. A glycidyl ester monomer means a glycidyl ester of  $\alpha,\beta$ -unsaturated carboxylic acid such as, e.g., acrylic acid, methacrylic acid, itaconic acid, and includes, e.g., glycidyl acrylate, glycidyl methacrylate,  
25 glycidyl itaconate. Glycidyl ester polymers include the glycidyl esters (co)polymer described in U.S. Patent 5,981,661. Suitable glycidyl ester copolymers may be made by conventional free radical initiated copolymerization.

Preferred graft bases for use in Component C, corresponding to the  
30 disclosure above with regard to B.2, include composite rubbers of from 1 to 30 wt. %, particularly preferably from 10 to 20 wt. %, silicone rubber and

from 99 to 70 wt. %, particularly preferably from 90 to 80 wt. %, butyl acrylate rubber (the indicated wt. % is here based in each case on the total weight of the graft base).

As discussed above, monomer B.1 of Component B comprises vinyl, or acrylic. These monomers may react with the functional shell polymer of Component C to form covalent bonds. . By limiting the amount of impact modifiers with a functional shell polymer, the resulting agglomerations, as discussed below, are found to have more free internal space and less covalent bonding, making them less dense, or "loose."

The microstructure of a thermoplastic composition is also highly dependent on the processing conditions. There is a growing interest for components called "core/shell" modifiers, which are small particles of crosslinked rubber phase surrounded by a compatibilizing shell. Core/shell modifiers have a fixed particle size and are often used as impact modifiers.

Core-shell elastomers are designed specifically to produce blends with good dispersion and toughness. The chemical composition and crosslink density of the elastic core determine the cavitation resistance of the particle whereas the composition of the shell is chosen to provide rigidity to the particles during processing and to impart compatibility with the matrix for good dispersion and adhesion. Toughening of thermoplastic using a core-shell impact modifier with a poly(butyl acrylate) (PBA) core and a polymethylmethacrylate (PMMA) shell has been reported before. The PMMA shell of the modifier is miscible with PC. Impact modifiers with varying particle size are used and their effect on impact strength is reported. The influence of rubber phase content and the incorporation of dual-sized particles are also presented.

Component C comprises about 60 to about 95 wt. % core, preferably 70 to about 90 wt. % core, with the remaining amount in Component C being the shell. The glass transition temperature of Component C is preferably -40°C or less, most preferably -50°C or less.

Component C may comprise about 1 wt.% to about 10 wt.% of the thermoplastic composition, preferably about 2 wt.% to about 7.5 wt.% of the

composition, wherein the wt.%, all instances, is based on total composition weight.

#### **Component D**

5            Optionally, the thermoplastic composition may include component D, a vinyl (co)polymer. Suitable as the vinyl (co)polymers include polymers of at least one monomer selected from the group of the vinyl aromatic compounds, vinyl cyanides (unsaturated nitriles), (meth)acrylic acid (C<sub>1</sub>-C<sub>8</sub>)-alkyl esters, unsaturated carboxylic acids as well as derivatives (such as anhydrides and  
10 imides) of unsaturated carboxylic acids. Particularly suitable are (co)polymers of:

D.1    from 50 to 99 parts by weight, preferably from 60 to 80 parts by weight, in particular from 72 to 78 parts by weight (based on component D) of vinyl aromatic compounds and/or vinyl aromatic compounds substituted on the  
15 ring, such as styrene,  $\alpha$ -methylstyrene, p-methylstyrene, p-chlorostyrene, and/or (meth)acrylic acid (C<sub>1</sub>-C<sub>8</sub>)-alkyl esters, such as methyl methacrylate, ethyl methacrylate, and

D.2    from 1 to 50 parts by weight, preferably from 20 to 40 parts by weight, in particular from 22 to 28 parts by weight (based on component D) of vinyl  
20 cyanides (unsaturated nitriles), such as acrylonitrile and methacrylonitrile, and/or (meth)acrylic acid (C<sub>1</sub>-C<sub>8</sub>)-alkyl esters, such as methyl methacrylate, n-butyl acrylate, tert-butyl acrylate, and/or unsaturated carboxylic acids, such as maleic acid, and/or derivatives, such as anhydrides and imides, of unsaturated carboxylic acids, for example maleic anhydride and N-  
25 phenylmaleimide.

The vinyl (co)polymers D are generally resin-like, thermoplastic and rubber-free. A preferred vinyl copolymer D is also a copolymer of D.1 styrene and D.2 acrylonitrile.

The (co)polymers according to D are known and can be prepared, for  
30 example, by radical polymerization, in particular by emulsion, suspension, solution or mass polymerization. The (co)polymers preferably have mean molecular weights Mw of from 15,000 to 200,000.



Component D may be present in the thermoplastic composition in an amount of 0 to 40%, preferably 5 to about 20% of the thermoplastic composition. Factors in choosing component D for use with the thermoplastic composition is (1) improvement in flow performance of the resulting thermoplastic composition, and (2) its miscibility, and its compatibility with the other components of the thermoplastic composition.

### **Component E**

The thermoplastic composition can optionally comprise one or more further commercially available polymer additives such as flame retardants, flame retardant synergists, anti-dripping agents (for example compounds of the substance classes of the fluorinated polyolefins, of the silicones as well as aramid fibers), lubricants and mold release agents (for example pentaerythritol tetrastearate), nucleating agents, stabilizers, antistatic agents (for example conductive blacks, carbon fibers, carbon nanotubes as well as organic antistatic agents such as polyalkylene ethers, alkylsulfonates or polyamide-containing polymers), as well as colorants and pigments, in amounts such that they do not impair the mechanical properties of the composition to the extent that the target property profile (no splintering fracture at  $-10^{\circ}\text{C}$ ) is no longer fulfilled.

Present in component E may be flame retardants, preferably phosphorus-containing flame retardants, in particular selected from the groups of the monomeric and oligomeric phosphoric and phosphonic acid esters, phosphonate amines and phosphazenes. Component E may also be a mixture of a plurality of components selected from one or more of these groups to be used as flame retardants. It is also possible to use other, preferably halogen-free phosphorus compounds that are not mentioned specifically here, on their own or in arbitrary combination with other, preferably halogen-free phosphorus compounds. Suitable phosphorus compounds include, for example: tributyl phosphate, triphenyl phosphate, tricresyl phosphate, diphenylcresyl phosphate, diphenyloctyl phosphate, diphenyl-2-ethylcresyl phosphate, tri-(isopropylphenyl)

phosphate, resorcinol-bridged di- and oligo-phosphate, and bisphenol A-bridged di- and oligo-phosphate. The use of oligomeric phosphoric acid esters derived from bisphenol A is particularly preferred. Phosphorus compounds that are suitable as flameproofing agents are known (see e.g. 5 EP-A 0 363 608, EP-A 0 640 655) or can be prepared by known methods in an analogous manner (e.g. Ullmanns Enzyklopädie der technischen Chemie, Vol. 18, p. 301 ff 1979; Houben-Weyl, Methoden der organischen Chemie, Vol. 12/1, p. 43; Beilstein Vol. 6, p. 177).

Component E may further contain additional optional additives 10 known to those in the art, such as, for example, antioxidants, UV absorbers, light absorbers, fillers, reinforcing agents, additional impact modifiers, plasticizers, optical brighteners, pigments, dyes, colorants, blowing agents, and combinations of any thereof.

In certain embodiments, a composition may comprise zero wt. % to 15 5.0 wt. % of Component E, more preferably, 0.02 wt. % to 1.64 wt. %, wherein the wt.%, all instances, is based on total composition weight.

### **Agglomeration**

As noted above, the thermoplastic composition comprises two or 20 more impact modifiers: an impact modifier having functional shell polymer, and an impact modifier having a component capable of reaction with functional shell polymer. When these impact modifiers are incorporated in a thermoplastic molding composition as described herein, the impact modifiers form loose agglomerates within the composition. It is believed 25 that the loose agglomerates are formed through reaction of the functional shell polymer. Notably, the spiral flow measurements of thermoplastic formulations with and without the impact modifier having a functional shell polymer indicated that the spiral flow was significantly lower in the formulation having an impact modifier having a functional shell polymer, a 30 discussed in the results below. Also described and shown in the examples below, loose agglomerates of particles are characterized by the grouping of impact modifiers that are connected together via epoxy groups of the

functional shell polymer, but in a loose manner that allows for spaces among and in between the particles. The loose manner is achieved through the apparent bonding, and likely reaction, of the impact modifiers through epoxy functionality, and with a combination of impact modifiers  
5 where one has a functional shell polymer, while the other does not have a functional shell polymer, but is capable of reaction with it.

Loose agglomerates are ones in which the particles of the impact modifier are viewable at a scale of 0.5 microns per inch as shown in the examples, and are seen aggregating with other particles in a loose  
10 manner. Loose agglomerates may further be characterized by the diameter of such agglomerates, along with the free space that exists within that diameter. In contrast, dense agglomerates are ones having relatively little open spaces within them. The formation of agglomerates was found to yield a wide range of free spaces within them. However, the free  
15 spaces of agglomerations created from the thermoplastic formulations were measured, and analyzed using statistical models. The diameter is measured according to the longest measurable diameter. The agglomerations that were observed to be dense agglomerations, included formulations having just one impact modifier, that modifier having a  
20 functional shell polymer. The agglomerations that were observed to be loose agglomerations, included formulations having two impact modifiers: one having a functional shell polymer, and one not having a functional shell polymer, but capable of reaction with it. The loose agglomerations measured herein range from 0.4 to 4.0 microns. The average diameter is  
25 1.0 +/- 0.5 micron. The free space, or free openings, of the loose agglomerations were measured to range from 20 - 60% overall, 75% of the free space measurements in the loose agglomerates were measured between 31 and 50%. It is believed that a significant amount of the agglomerations, namely 50%, should be within the range of 31- 60% free  
30 space, in order to achieve the benefits outlined below.

Loose agglomerates of the rubber particles have been found to have significant benefits. It leads to the formation of large loose rubber

clusters or loose rubber aggregates that will scatter light, giving the resulting thermoplastic formulation a low gloss appearance. It also provides low temperature ductility; as the temperature drops and rubber particles become more brittle and less elastic, the loose agglomerates  
5 have been found to provide additional low temperature ductility beyond the ductility through use of any one of the impact modifiers alone.

### **Molding Compositions**

The thermoplastic molding compositions according to the invention  
10 can be prepared, for example, by mixing the constituents in a known manner and melt compounding and melt extruding the mixture at temperatures of from 200°C to 340°C, preferably from 240 to 300°C, in conventional devices such as internal kneaders, extruders and twin-shaft screws.

15 Mixing of the individual constituents can be carried out, in known manner, either in succession or simultaneously, either at about 20°C (room temperature) or at a higher temperature.

The present invention also provides a process for the preparation of the molding compositions and the use of the molding compositions in the  
20 production of molded parts.

The molding compositions according to the present invention can be used, for example, in the production of molded parts of any kind. These can be produced, for example, by injection molding, extrusion and blow molding processes. A further form of processing is the production of  
25 molded parts by deep-drawing from previously produced sheets or films.

Examples of such molded parts include films, profiles, casing parts of any kind, for example for domestic appliances such as juice extractors, coffee makers, mixers; for office equipment such as monitors, flat screens, notebooks, printers, copiers; sheets, tubes, conduits for electrical  
30 installations, windows, doors and further profiles for the construction sector (interior fitting and external applications) as well as parts for electronics and electrical engineering, such as switches, plugs and sockets, as well as

bodywork and interior components for commercial vehicles, in particular for the automotive sector.

The thermoplastic molding compositions according to the invention can also be used, for example, in the production one or more of the following molded parts or moldings: Parts for the interior finishing of railway vehicles, ships, aircraft, buses and other motor vehicles, casings for electrical devices containing small transformers, casings for devices for disseminating and transmitting information, casings and coverings for medical devices, massage devices and casings therefor, toy vehicles for children, prefabricated wall panels, casings for security devices, heat-insulated transport containers, moldings for sanitary and bathroom fittings, cover grids for ventilator openings, and casings for garden equipment. Other molded parts and/or moldings are also contemplated.

The molding compositions according to the present invention are particularly suitable for the production of automotive interior components and bodywork parts which must withstand the effects of light, heat and optionally weathering.

The non-limiting and non-exhaustive examples that follow are intended to further describe various non-limiting and non-exhaustive embodiments without restricting the scope of the embodiments described in this specification.

### **Examples**

In the Examples below, the following materials were used:

- |    |             |  |
|----|-------------|--|
| 25 | Component A | a linear polycarbonate based on bisphenol A having a weight-average molecular weight MW of 25,000 g/mol (determined by GPC)  |
| 30 | Component B | a graft polymer characterized by core-shell morphology, consisting of about 70 to about 90% core, the remainder being shell, the core comprising about 20 to about 60% silicone rubber and about 40 to about 80% butyl acrylate rubber, prepared by emulsion polymerization, the silicone rubber portion |

		comprises at least 50% organosiloxane; the shell comprises styrene acrylonitrile copolymer
5	Component C	a graft polymer characterized by core-shell morphology, consisting of about 70 to about 90% core, the remainder being shell, the core comprising about 10 to about 20 wt. %, silicone rubber and from about 80 to about 90 wt. %, butyl acrylate rubber, prepared by emulsion polymerization, the silicone rubber portion comprises at least 50%
10		organosiloxane; the shell comprises styrene acrylonitrile copolymer and epoxy functionality, the epoxy functionality being GMA
15	Component D	Styrene/acrylonitrile copolymer having a styrene/acrylonitrile weight ratio of 76:24 wt. % and a mean molecular weight of 100,000 g/mol (measured by GPC in dimethylformamide at 20° C)
	Component E1	UV light stabilizer, commercially available from BASF as Tinuvin 329
	Component E2	release agent pentaerythritol tetrastearate
20	Component E3	octadecyl-3-(3,5-di-tert.butyl-4-hydroxyphenyl)-propionate, a thermal stabilizer, commercially available from Ciba Specialty Chemicals as Irganox 1076
25	Component E4	hydrolytic stabilizer tris(2,4-ditert-butylphenyl) phosphite, commercially available from Ciba Specialty Chemicals as Irganox 168;

The following thermoplastic compositions were created, as described in Table 1. Unless otherwise indicated, all values in Table 1 are listed in parts by weight. The results of the samples are summarized in

30 Table 2.

Table 1

Component	Sample #	57	58	59	60	61	62	63	64	65
Component A		70.50	70.79	68.36	72.49	68.36	73.36	70.5	68.36	73.36
	Core T <sub>g</sub> (°C)									
Component B	-58	8.5	12.6	5.0	5.0	15.0	7.4	8.5	10.0	10.0
Component C	-50	4.3	0.0	10.0	5.9	0.0	2.6	4.3	5.0	0.0
Component D		15	15	15	15	15	15	15	15	15
Component E1		0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8
Component E2		0.74	0.74	0.74	0.74	0.74	0.74	0.74	0.74	0.74
Component E3		0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02
Component E4		0.08	0.08	0.08	0.08	0.08	0.08	0.08	0.08	0.08

Table 2

Sample		Test	Units	57	58	59	60	61	62	63	64	65
Mechanical Properties												
Notched IZOD impact energy	@ -20°C	ISO 180/1A (2000)	kJ/m <sup>2</sup>	51.0	71.5	36.1	30.1	77.3	48.9	49.6	48.5	62.6
Break type	@ -20°C	ISO 180/1A (2000)		10par	10par	10par	5par 1hin 4C	10par	10par	10par	10par	10par
Multi-axial impact total energy	@ -30°C	ASTM D3763B	J	50.0	57.8	50.1	55.7	53.4	60.6	59.1	53.0	60.6
Break type	@ -30°C	ASTM D3763B		5D	5D	5B	5B	4D 1B	5D	4D 1B	5D	1D 4B
Tensile elongation at break		ISO 527	%	106	123	97	115	136	111	111	113	118
Gloss												
Specular gloss at 60°		ASTM D523		70	103	54	60	104	86	77	73	104
Processing Properties												
Spiral flow (0.100")	@ 260°C	See below	in	20.3	22.3	21.5	21.3	22.9	20.8	20.8	20.4	21.6
Spiral flow (0.100")	@ 280°C	See below	in	24.8	26.9	27.8	26.3	27.5	25.0	25.0	24.8	26.3



As shown in the examples given above, when the thermoplastic composition comprises both a first impact modifier characterized by core-shell morphology and comprising epoxy functionality, and a second impact modifier comprising a component capable of reaction with epoxy functionality, both the low temperature ductility is improved and the composition had low gloss.

As noted above, the impact strength was measured in accordance with ASTM D3763. This was performed at room temperature and -30C, using specimens 1/8" inch in thickness. For each sample, five different specimens were tested to determine whether each would experience a ductile (D) or a brittle (B) failure. A ductile failure is one where the specimen deformed plastically before fracturing, and where the specimen is without cracks radiating more than 10 mm beyond the center of the impact point. A brittle failure is one where the specimen test area is broken into two or more pieces, with sharp edges and thus exhibits little plastic flow. The best measurements for low temperature ductility noted in Table 2, was a 5D rating (meaning each of the 5 specimen exhibited ductile failure), which was achieved in only four samples: 57, 58, 62 and 64. Several other samples (59 and 60) achieved a 5B rating, which is not desired.

The gloss, as shown by the specular gloss measurements at 60°, is significantly lower in compositions having each of these components as well. Samples 57, 59, 60, 62, 63 and 64 were each shown to have low gloss. Surprisingly, each of these samples were from compositions including both Component B and Component C, while the samples from compositions having just one impact modifier all had higher gloss. Finally, the above samples were each shown to be sufficiently flowable to be used as a molding composition.

Spiral flow is measured using a Roboshot injection molding machine applying the designated molding conditions for mold and melt temperature and measure how far it can push the material. The mold temperature is 80 C,

and the melt temperature is indicated in Table 2. The mold is subject to a high pressure of 18,000 psi for 3 seconds, then a hold pressure of 10,000 psi for 6 seconds, and then cooling for 20 seconds at the back pressure of 800 psi. The screw speed is 100 rpm. The injection speed is 4 inches per second. The decompression distance is 0.10 inches. The maximum pack velocity is 0.50 inches per second. The position transfer is 0.10 inches. The shot size is designed to maintain a 0.25 inch cushion. The clamp tonnage equals 110 short tons. The length of the spiral flow is measured in inches.

In addition to the above testing, the agglomerates of several samples were characterized through the use of Atomic Force Microscopy (AFM). The AFM images were obtained in air with a commercial scanning probe microscope (Nanoscope IIIa, Digital Instruments, Santa Barbara, California) operated in the tapping mode. Height and phase images were recorded simultaneously. Measurements were performed at ambient conditions using rectangular-type Si probes with spring constants of  $50 \text{ Nm}^{-1}$  and resonance frequencies in the 284 –362 kHz range. The tip radius was 10 nm. The results are discussed below. AFM is powerful technique that can provide direct mapping of surface morphology with nanometer resolution. Further, the phase contrast in tapping mode AFM often reflects differences in the properties of individual components of heterogeneous materials, and is useful for compositional mapping in polymer blends and copolymers, and heterogeneity mapping in polymer coatings. Additionally, AFM requires no specific sample preparation procedure, can be operated in ambient condition and provides information about the sample surface in a relatively nondestructive way, it is very suitable to use this technique to monitor the change of the surface feature of the same sample with the time of the exposure.

In a comparative sample, a thermoplastic formulation was prepared comprising Components A, D and E as described above, and 10 wt. % of Component B, with no Component C. Using AFM at a scale of about 0.5

microns per inch, the particles of Component B are visible in darker color, while Components A and D are visible in a lighter color. The particles of Component B can be seen as a dispersion; the particles do not form agglomerates.

5           In a sample comprising an inventive composition, a thermoplastic formulation was prepared comprising Components A, D and E as described above, and 10 wt. % of Component B and 5% of Component C. A molded part was made therefrom, under the following conditions: the composition was heated to 280 – 305 °C for melt temperature, and then was molded at around  
10   80 °C, with the injected speed range from 0.4 – 1.2 in/ sec. Using AFM at a scale of about 0.5 microns per inch, the particles of Components B and C are viewable at this scale in a darker color, with the remainder of the components in a lighter color, and are seen combining into loose agglomerates. A total of 77 agglomerates from 5 images taken from slices of the molded parts were  
15   analyzed. The range of diameters measured, according to the longest measurable diameter, was 0.4-4.0 microns. The average diameter was 1.0 +/- 0.5 microns. The free space, or free openings, of the loose agglomerations were measured to be 20 - 60% overall, 75% of the free space measurements in the loose agglomerates were measured between 31 and  
20   50%. The median free space was measured to be 36%, and the median 50% of measurements were between 31 and 39%.

          In another comparative example, a thermoplastic formulation was prepared using Components A, D and E as described above, and 10% of Component C, and no Component B. Using AFM at a scale of about 0.5  
25   microns per inch, the particles of Component C were observed to form dense agglomerates, and the individual impact modifier particles can no longer be seen. It is believed that the epoxy functionality has worked to tightly bond the particles with each other to form such masses. The range in size of the tight agglomerates was 0.6-3.6 micron, with an average of 1.5 +/-

0.7 microns. The free space of the dense agglomerates was measured to be 0 – 39%, with 75% of the measurements between 0 and 26%. The median free space was measured to be 22.5%, with the median 50% of measurements between 13.8% and 26%.

5 Aspects of the thermoplastic compositions disclosed herein include:

A thermoplastic composition comprising:

A) a thermoplastic resin;

10 B) an impact modifier capable of reaction with a functional shell polymer, that does not comprise a functional shell polymer; and

C) an impact modifier characterized by core-shell morphology and comprising a functional shell polymer.

A thermoplastic composition comprising:

15 - a thermoplastic resin; and

- loose agglomerations of particles;

wherein at least 50% of the loose agglomerations comprise open spaces that measure 31 to 60 % by area of the loose agglomeration,

20 and wherein the loose agglomerations of particles comprise particles characterized by core-shell morphology.

Any of the thermoplastic compositions disclosed herein, wherein the thermoplastic resin comprises a polyester selected from the group consisting of polycarbonate, polyethylene terephthalate and polybutylene terephthalate.

25

Any of the thermoplastic compositions disclosed herein, wherein the thermoplastic resin comprises about 40 to about 90 wt. % of the composition, preferably about 60 to about 80 wt. %, most preferably about 65 to about 75 wt. %.

Any of the thermoplastic compositions disclosed herein, wherein the loose agglomerations comprise Component B: an impact modifier and Component C: a second impact modifier.

5

Any of the thermoplastic compositions disclosed herein, wherein Component B is characterized by core-shell morphology.

Any of the thermoplastic compositions disclosed herein, wherein Component B or Component C comprises a core that does not include carbon-carbon double-bonds.

10

Any of the thermoplastic compositions disclosed herein, wherein Component B comprises a siloxane.

15

Any of the thermoplastic compositions disclosed herein, wherein Component B comprises a graft base, that comprises 10 to 70 wt.%, particularly preferably from 20 to 60 wt.%, silicone rubber.

Any of the thermoplastic compositions disclosed herein, wherein Component B comprises acrylic.

20

Any of the thermoplastic compositions disclosed herein, wherein Component B comprises an impact modifier capable of reaction with epoxy functionality, that does not comprise epoxy functionality.

25

Any of the thermoplastic compositions disclosed herein, wherein Component B or Component C comprises acrylate.

Any of the thermoplastic compositions disclosed herein, wherein Component B or Component C comprises methyl methacrylate.

- 5 Any of the thermoplastic compositions disclosed herein, wherein the functional shell polymer of Component C is epoxy functionality.

Any of the thermoplastic compositions disclosed herein, wherein the epoxy functionality of Component C is glycidyl (meth)acrylate.

- 10 Any of the thermoplastic compositions disclosed herein, wherein Component B or Component C has a glass transition temperature of  $-40^{\circ}\text{C}$  or less, preferably  $-50^{\circ}\text{C}$  or less.

- 15 Any of the thermoplastic compositions disclosed herein, wherein Component B or Component C comprises about 60 to about 95 wt. % core, preferably about 70 to about 80 wt. % core, as a percentage of the total weight of the impact modifier's core and shell.

- 20 Any of the thermoplastic compositions disclosed herein, wherein Component B is present in the composition in an amount of about 5 to about 20 wt. %, preferably about 7.5 to about 15 wt. %.

- 25 Any of the thermoplastic compositions disclosed herein, wherein Component C is present in the composition in an amount of about 1 to about 10 wt. %, preferably 2 to about 7.5 wt. %.

Any of the thermoplastic compositions disclosed herein, further comprising Component D: a vinyl (co)polymer.

Any of the thermoplastic compositions disclosed herein, wherein the vinyl (co)polymer is styrene acrylonitrile.

- Any of the thermoplastic compositions disclosed herein, wherein Component
- 5 D comprises about 5 to about 20 wt. % of the thermoplastic composition.

- Any of the thermoplastic compositions disclosed herein, further comprising Component E: at least one additive selected from group consisting of: flame retardants, flame retarding synergists, anti-dripping agents, antioxidants, UV
- 10 absorbers, light absorbers, fillers, reinforcing agents, additional impact modifiers, lubricants, plasticizers, optical brighteners, pigments, dyes, colorants, anti-static agents, mold-release agents, blowing agents, and combinations of any thereof.

- 15 Any of the thermoplastic compositions disclosed herein, wherein Component E comprises about 0.02 to about 1.64 wt. % of the thermoplastic composition.

- Any of the thermoplastic compositions disclosed herein, wherein Component B and Component C form loose agglomerations of particles, wherein at least
- 20 50% of the loose agglomerations comprise open spaces that measure 31 to 60 % by area of the loose agglomeration.

- Any of the thermoplastic compositions disclosed herein, wherein the loose agglomerations comprise particles having a diameter between 0.4 and 4.0
- 25 microns.

A molded part comprising any of the thermoplastic compositions disclosed herein.

A process for producing a molded part comprising any of the thermoplastic compositions disclosed herein, the process comprising at least one of an injection molding, an extrusion and a blow molding process.

- 5 A molded part comprising a thermoplastic resin and loose agglomerations of particles, wherein at least 50% of the loose agglomerations comprise open spaces that measure 31 to 60 % by area of the loose agglomeration, and wherein the loose agglomerations of particles comprise particles characterized by core-shell morphology.

10

A process for producing a molded part having a thermoplastic resin and loose agglomerations of particles, wherein at least 50% of the loose agglomerations comprise open spaces that measure 31 to 60 % by area of the loose agglomeration, and wherein the loose agglomerations of particles comprise particles characterized by core-shell morphology, the process comprising at least one of an injection molding, an extrusion and a blow molding process.

15

In addition, the following thermoplastic molding compositions are disclosed:

40 – 90 % thermoplastic resin,

5 – 20 % Component B,

20 1 – 10 % Component C,

5 – 20% Component D, and

0.02 – 1.64 % Component E.

40 – 90 % thermoplastic resin,

25 7.5 – 15 % Component B,

1 – 10 % Component C,

5 – 20% Component D, and



0.02 – 1.64 % Component E.

40 – 90 % thermoplastic resin,  
5 – 20 % Component B,  
5 2 – 7.5 % Component C,  
5 – 20% Component D, and  
0.02 – 1.64 % Component E.

40 – 90 % thermoplastic resin,  
10 7.5 – 15 % Component B,  
2 – 7.5 % Component C,  
5 – 20% Component D, and  
0.02 – 1.64 % Component E.

15 60 – 80 % thermoplastic resin,  
5 – 20 % Component B,  
1 – 10 % Component C,  
5 – 20% Component D, and  
0.02 – 1.64 % Component E.

20 60 – 80 % thermoplastic resin,  
7.5 – 15 % Component B,  
1 – 10 % Component C,  
5 – 20% Component D, and  
25 0.02 – 1.64 % Component E.

60 – 80 % thermoplastic resin,  
5 – 20 % Component B,  
2 – 7.5 % Component C,

5 – 20% Component D, and  
0.02 – 1.64 % Component E.

60 – 80 % thermoplastic resin,  
5 7.5 – 15 % Component B,  
2 – 7.5 % Component C,  
5 – 20% Component D, and  
0.02 – 1.64 % Component E.

10 65 – 75 % thermoplastic resin,  
5 – 20 % Component B,  
1 – 10 % Component C,  
5 – 20% Component D, and  
0.02 – 1.64 % Component E.

15  
65 – 75 % thermoplastic resin,  
7.5 – 15 % Component B,  
1 – 10 % Component C,  
5 – 20% Component D, and  
20 0.02 – 1.64 % Component E.

65 – 75 % thermoplastic resin,  
5 – 20 % Component B,  
2 – 7.5 % Component C,  
25 5 – 20% Component D, and  
0.02 – 1.64 % Component E.

65 – 75 % thermoplastic resin,  
7.5 – 15 % Component B,

2 – 7.5 % Component C,  
5 – 20% Component D, and  
0.02 – 1.64 % Component E.

**WHAT IS CLAIMED IS:**

Claim 1. A thermoplastic composition comprising:

- A) a thermoplastic resin;
- B) an impact modifier capable of reaction with a functional shell polymer, that does not comprise a functional shell polymer; and
- C) an impact modifier characterized by core-shell morphology and comprising a functional shell polymer.

Claim 2. The thermoplastic composition of Claim 1, wherein the thermoplastic resin comprises a polyester selected from the group consisting of polycarbonate, polyethylene terephthalate and polybutylene terephthalate.

Claim 3. The thermoplastic composition of Claim 1, wherein the thermoplastic resin comprises about 40 to about 90 wt. % of the composition, preferably about 60 to about 80 wt. %, most preferably about 65 to about 75 wt. %.

Claim 4. The thermoplastic composition of Claim 1, wherein Component B is characterized by core-shell morphology.

Claim 5. The thermoplastic composition of Claim 1, wherein Component B or Component C comprises a core that does not include carbon-carbon double-bonds.

Claim 6. The thermoplastic composition of Claim 1, wherein Component B comprises a siloxane.

Claim 7. The thermoplastic composition of Claim 1, wherein Component B further comprises a graft base, the graft base comprising 10 to 70 wt.%, particularly preferably from 20 to 60 wt.%, silicone rubber.

Claim 8. The thermoplastic composition of Claim 1, wherein Component B comprises acrylic.

Claim 9. The thermoplastic composition of Claim 1, wherein Component B comprises an impact modifier capable of reaction with epoxy functionality, that does not comprise epoxy functionality.

Claim 10. The thermoplastic composition of Claim 1, wherein Component B or Component C comprises acrylate.

Claim 11. The thermoplastic composition of Claim 1, wherein Component B or Component C comprises methyl methacrylate.

Claim 12. The thermoplastic composition of Claim 1, wherein the functional shell polymer of Component C is epoxy functionality.

Claim 13. The thermoplastic composition of Claim 12, wherein the epoxy functionality of Component C is glycidyl (meth)acrylate.

Claim 14. The thermoplastic composition of Claim 1, wherein Component B or Component C has a glass transition temperature of -40°C or less, preferably -50°C or less.

Claim 15. The thermoplastic composition of Claim 1, wherein Component B or Component C comprises about 60 to about 95 wt. % core, preferably about

70 to about 80 wt. % core, as a percentage of the total weight of the impact modifier's core and shell.

Claim 16. The thermoplastic composition of Claim 1, wherein Component B is present in the composition in an amount of about 5 to about 20 wt. %, preferably about 7.5 to about 15 wt. %.

Claim 17. The thermoplastic composition of Claim 1, wherein Component C is present in the composition in an amount of about 1 to about 10 wt. %, preferably 2 to about 7.5 wt. %.

Claim 18. The thermoplastic composition of Claim 1, further comprising Component D: a vinyl (co)polymer.

Claim 19. The thermoplastic composition of Claim 18, wherein the vinyl (co)polymer is styrene acrylonitrile.

Claim 20. The thermoplastic composition of Claim 18, wherein Component D comprises about 5 to about 20 wt. % of the thermoplastic composition.

Claim 21. The thermoplastic composition of Claim 1, further comprising Component E: at least one additive selected from group consisting of: flame retardants, flame retarding synergists, anti-dripping agents, antioxidants, UV absorbers, light absorbers, fillers, reinforcing agents, additional impact modifiers, lubricants, plasticizers, optical brighteners, pigments, dyes, colorants, anti-static agents, mold-release agents, blowing agents, and combinations of any thereof.

Claim 22. The thermoplastic composition of Claim 21, Component E comprises about 0.02 to about 1.64 wt. % of the thermoplastic composition.

Claim 23. The thermoplastic composition of Claim 1, wherein Component B and Component C form loose agglomerations of particles, wherein at least 50% of the loose agglomerations comprise open spaces that measure 31 to 60 % by area of the loose agglomeration.

Claim 24. The thermoplastic composition of Claim 23, wherein the loose agglomerations comprise particles having a diameter between 0.4 and 4.0 microns.

Claim 25. A molded part comprising the thermoplastic composition of Claim 1.

Claim 26. A process for producing a molded part comprising the thermoplastic composition of Claim 1, the process comprising at least one of an injection molding, an extrusion and a blow molding process.

Claim 27. A thermoplastic composition comprising:

- a thermoplastic resin; and
- loose agglomerations of particles;

wherein at least 50% of the loose agglomerations comprise open spaces that measure 31 to 60 % by area of the loose agglomeration, and wherein the loose agglomerations of particles comprise particles characterized by core-shell morphology.

Claim 28. The thermoplastic composition of Claim 27, wherein the thermoplastic resin comprises a polyester selected from the group consisting of polycarbonate, polyethylene terephthalate and polybutylene terephthalate.

Claim 29. The thermoplastic composition of Claim 27, wherein the thermoplastic resin comprises about 40 to about 90 wt. % of the composition,

preferably about 60 to about 80 wt. %, most preferably about 65 to about 75 wt. %.

Claim 30. The thermoplastic composition of Claim 27, wherein the loose agglomerations comprise Component B: an impact modifier and Component C: a second impact modifier.

Claim 31. The thermoplastic composition of Claim 30, wherein Component B does not comprise a functional shell polymer.

Claim 32. The thermoplastic composition of Claim 30, wherein Component C comprises a functional shell polymer.

Claim 33. The thermoplastic composition of Claim 30, wherein Component B is characterized by core-shell morphology.

Claim 34. The thermoplastic composition of Claim 30, wherein Component B or Component C comprises a core that does not include carbon-carbon double-bonds.

Claim 35. The thermoplastic composition of Claim 30, wherein Component B comprises a siloxane.

Claim 36. The thermoplastic composition of Claim 30, wherein the graft base of Component B comprises 10 to 70 wt.%, particularly preferably from 20 to 60 wt.%, silicone rubber.

Claim 37. The thermoplastic composition of Claim 30, wherein Component B comprises acrylic.



Claim 38. The thermoplastic composition of Claim 30, wherein Component B comprises an impact modifier capable of reaction with epoxy functionality, that does not comprise epoxy functionality.

Claim 39. The thermoplastic composition of Claim 30, wherein Component B or Component C comprises acrylate rubber.

Claim 40. The thermoplastic composition of Claim 30, wherein Component B or Component C comprises methyl methacrylate.

Claim 41. The thermoplastic composition of Claim 30, wherein the functional shell polymer of Component C is epoxy functionality.

Claim 42. The thermoplastic composition of Claim 30, wherein the epoxy functionality of Component C is glycidyl (meth)acrylate.

Claim 43. The thermoplastic composition of Claim 30, wherein Component B or Component C has a glass transition temperature of  $-40^{\circ}\text{C}$  or less, preferably  $-50^{\circ}\text{C}$  or less.

Claim 44. The thermoplastic composition of Claim 30, wherein Component B or Component C comprises about 60 to about 95 wt. % core, preferably about 70 to about 80 wt. % core, as a percentage of the total weight of the impact modifier's core and shell.

Claim 45. The thermoplastic composition of Claim 30, wherein Component B is present in the composition in an amount of about 5 to about 20 wt. %, preferably about 7.5 to about 15 wt. %.

Claim 46. The thermoplastic composition of Claim 30, wherein Component C is present in the composition in an amount of about 1 to about 10 wt. %, preferably 2 to about 7.5 wt. %.

Claim 47. The thermoplastic composition of Claim 27, further comprising Component D: a vinyl (co)polymer.

Claim 48. The thermoplastic composition of Claim 47, wherein the vinyl (co)polymer is styrene acrylonitrile.

Claim 49. The thermoplastic composition of Claim 47, wherein Component D comprises about 5 to about 20 wt. % of the thermoplastic composition.

Claim 50. The thermoplastic composition of Claim 27, further comprising Component E: at least one additive selected from group consisting of: flame retardants, flame retarding synergists, anti-dripping agents, antioxidants, UV absorbers, light absorbers, fillers, reinforcing agents, additional impact modifiers, lubricants, plasticizers, optical brighteners, pigments, dyes, colorants, anti-static agents, mold-release agents, blowing agents, and combinations of any thereof.

Claim 51. The thermoplastic composition of Claim 50, Component E comprises about 0.02 to about 1.64 wt. % of the thermoplastic composition.

Claim 52. The thermoplastic composition of Claim 27, wherein the loose agglomerations comprises particles having a diameter between 0.4 and 4.0 microns.

Claim 53. A molded part comprising the thermoplastic composition of Claim 27.

Claim 54. A process for producing a molded part comprising the thermoplastic composition of Claim 27, the process comprising at least one of an injection molding, an extrusion and a blow molding process.

Claim 55. A molded part comprising:

- a thermoplastic resin; and
- loose agglomerations of particles;

wherein at least 50% of the loose agglomerations comprise open spaces that measure 31 to 60 % by area of the loose agglomeration, and wherein the loose agglomerations of particles comprise particles characterized by core-shell morphology.

Claim 56. A process for producing a molded part of Claim 55, the process comprising at least one of an injection molding, an extrusion and a blow molding process.

# INTERNATIONAL SEARCH REPORT

International application No  
PCT/US2015/064747

<b>A. CLASSIFICATION OF SUBJECT MATTER</b> INV. C08L69/00 C08L67/00 C08L51/00 ADD.		
According to International Patent Classification (IPC) or to both national classification and IPC		
<b>B. FIELDS SEARCHED</b> Minimum documentation searched (classification system followed by classification symbols) C08L		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) EPO-Internal		
<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2008/057355 A2 (BAYER MATERIALSCIENCE LLC [US]; ROGUNOVA MARINA [US]; MASON JAMES P [U] 15 May 2008 (2008-05-15) examples; tables 1,2 page 19, line 10 - line 14 -----	1-56
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<div style="display: flex; justify-content: space-between; align-items: center;"> <div> <input type="checkbox"/> Further documents are listed in the continuation of Box C.         </div> <div> <input checked="" type="checkbox"/> See patent family annex.         </div> </div>		
* Special categories of cited documents :		
<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier application or patent but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"&amp;" document member of the same patent family</p> </div> </div>		
Date of the actual completion of the international search  <div style="text-align: center; font-size: 1.2em;">29 August 2016</div>	Date of mailing of the international search report  <div style="text-align: center; font-size: 1.2em;">05/09/2016</div>	
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer  <div style="text-align: center; font-size: 1.2em;">Mettler, Rolf-Martin</div>	

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2015/064747

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