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(54) Title: LOW TEMPERATURE IMPACT MODIFIERS WITH GOOD TRANSPARENCY AND WEATHERABILITY

(57) Abstract: Disclosed are a graft copolymer with core-shell structure, a process for the preparation of the graft copolymers, a process for producing a thermoplastic resin, and a mixture of the graft copolymer with core-shell structure. The core is produced by several steps of a successive emulsion polymerization of one or more monomers in the presence of one or more plasticizers, the plasticizer content being 10 to 80%and the monomer content being 90 to 10%. The graft copolymer with core-shell structure ensures impact modifiers for low temperature applications with good transparency and weatherability.

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Low temperature impact modifiers with good transparency and weatherability

FIELD OF THE INVENTION

The invention relates to the field of impact modifiers, more specifically, to impact modifiers for low temperature applications with good transparency and weatherability.

BACKGROUND

Impact modifiers are crucial additives for many applications and plastics, especially for PVC window profiles and in some regions even for pipes. Impact resistance or impact strength is defined as "the ability of a material or structure made of it to withstand the application of a sudden load without failure."

PVC as a pure polymer already has good impact strength. In some cases, however, it is necessary to improve the impact resistance by adding impact modifiers. The impact resistance of the PVC end product depends on many factors, e. g. on temperature.

Various types of impact modifiers are commercially available. A distinction is made between impact modifiers with a core-shell structure and those with a network structure, the latter not being the subject of the present invention. An advantage of this core-shell technology is that it prevents the product from being destroyed by shear during processing. The disadvantage of the rubbery core is its stickiness. To reduce stickiness, various monomers are grafted onto the surface of the core. This grafted shell has two functions:

- It prevents the modifier particles from sticking to each other and
- supports better dispersion and compatibility in the PVC matrix.

Core-shell impact modifiers based on acrylate (AIM) are produced by emulsion polymerization with radical initiators [S.-K. Ko; “Darstellung von Core-Shell Polymeren mit Hilfe polymerer Azo-Initiatoren“(Synthesis of core-shell polymers with the aid of polymeric azo initiators), H. Utz Verlag Wissenschaft, Germany H. Utz Verlag Wissenschaft, Germany (1998) p. 10]. Suitable monomers are combined and polymerized in several steps. Crosslinking agents are added to form the crosslinked rubbery phase of the core, which generally has a glass transition temperature Tg of about -45℃ and above. They are characterized by good properties in terms of impact resistance, transparency and weatherability.

Methyl methacrylate (MMA) butadiene styrene modifiers (MBS) also have a core-shell structure. As the name suggests, they are made by copolymerizing styrene, butadiene and MMA, which are present in the shell analogously to the AIMs. The glass transition temperature Tg of MBS types is significantly lower than that of AIMs. They are at -55℃ [DE 2726256 C2] and below (up to -70℃ [Technical information - Clearstrength E-920; http://www.arkema-inc.com/tds/1325.pdf; downloaded (03/2014)]). The MBS modifiers are therefore perfect for low temperature applications. However, they have a negative impact on transparency and are not suitable for outdoor applications that require weatherability.

For the sake of completeness, core-shell modifiers which contain crosslinked silicones in the core are also to be mentioned in this context [US5969045]. They combine good weatherability with a very low glass transition temperature Tg, which is significantly lower than that of AIMs.

BRIEF SUMMARY OF THE DISCLOSURE

According to the above described defects, the purpose of the present invention is providing impact modifiers for low temperature applications with good transparency and weatherability.

A technical solution of the present invention to solve the technical problems is as follows:

Graft copolymer with core-shell structure, characterized in that the core is produced by several steps of a successive emulsion polymerization of one or more monomers in the presence of one or more plasticizers, the plasticizer content being 10 to 80% and the monomer content being 90 to 10%.

Graft copolymer with core-shell structure, characterized in that the monomers are selected from the group C1-C12-alkyl acrylates, C1-C12-alkyl methacrylates, styrene and its substituted derivatives as well as vinyl ethers, vinyl esters or vinyl propionate

Graft copolymer with core-shell structure, characterized in that the plasticizers are selected from the group consisting of azelate, phenyl alkylsulfonic acid, azelates, benzoates, chlorinated paraffins, citrates, epoxies, ricinolates, phosphates, valerates, phthalates, sebacates, terephthalates and trimellitates.

Graft copolymer with core-shell structure, characterized in that the plasticizers are selected from the group dibutyl adipate, di (2-ethylhexyl) adipate, di-decyl adipate, di-i-nonyl adipate, di-i-octyl adipate, di-i-tridecyl adipate, Di-n-octyl adipate, dibutylazelate, di (2-ethylhexyl) azelate, di-decylazelate, di-i-nonylazelate, di-i-octylazelate, di-i-tridecylazelate, di-n-octylazelate, dibutyl sebazate, di (2- ethylhexyl) sebazate, di-decyl sebazate, di-i-nonyl sebazate, di-i-octyl sebazate, di-i-tridecyl sebazate and di-n-octyl sebazate

Process for the preparation of graft copolymers, characterized in that

a. Forming a latex from rubber-like polymer particles with a glass transition temperature Tg <-20℃ and a particle size of 50 to 300 nm in diameter is formed by emulsion polymerization
b. Forming, by sequential emulsion polymerization in the presence of the rubber-like polymer particle latex under conditions where substantially no new polymer particles are formed, a polymeric latex of the first core / intermediate shell, the intermediate polymer shell has
    a. a glass transition temperature Tg> 50℃,
    b. are predominantly formed from units derived from methyl methacrylate, and
    c. about 5% to about 20% by weight of the first core / intermediate shell polymer particles;
c. Agglomerating the latex of the polymer particles of the first core / intermediate sheath to form a latex of the agglomerated particles with a diameter of at least 150 nm, the solids content of the latex of the polymer particles of the first core / intermediate sheath being not higher than 40% and the solids content not higher than Is 30%;
d. Forming a hard polymer encapsulation shell having a glass transition temperature of at least 60℃ in a final core / shell polymer by sequential emulsion polymerization on the agglomerated particles under conditions where essentially no new polymer particles are formed, the encapsulation shell
    a. are predominantly formed from units derived from methyl methacrylate
    b. 5 to 20% by weight of the final core-shell polymer, the total shell content being not less than 14% by weight of the final core-shell polymer, the sequential emulsion polymerization being carried out in the latex of the agglomerated particles and the final Core-shell polymer remain in latex form; and, if desired,
e. isolating the final core-shell polymer.

Method comprises the final core-shell polymer is isolated by (a) spray drying or (b) coagulating, preferably by adding an aqueous solution of an inorganic acid salt.

A process for producing a thermoplastic resin comprising:

a. Forming a final core-shell polymer by the method ; and
b. Mixing, for example in an extruder or on a heated multi-roll mill, the final core-shell polymer with a thermoplastic resin under heat and shear conditions sufficient to cause the final core-shell polymer to be dispersed in particle domains equivalent in size the core / intermediate shell polymer or polymer particles prior to agglomeration; and

c. optionally processing the pre-stressed thermoplastic resin into an article by extrusion, calendering or injection molding.

Method of process for producing a thermoplastic resin, wherein the thermoplastic resin is a homo- or copolymer of vinyl chloride, a chlorinated PVC or a homo- or copolymer of methyl methacrylate or a technical resin such as a polyester of terephthalic acid and an aliphatic glycol, a polyamide, a polycarbonate B. a polyglutarimide, an acrylonitrile-butadiene-styrene resin or a mixture of at least two such resins.

Mixture comprising 60 to 99% by weight of a thermoplastic polymer and 1 to 40% by weight of the core-shell graft copolymer or produced by a process .

Mixture further contains one or more constituents: lubricant, processing aid, rheology modifier, dye, pigment, flame retardant, heat stabilizer, antioxidant, antiozonant, ultraviolet stabilizer, mold release agent, reinforcing or non-reinforcing filler.

DETAILED DESCRIPTION OF EMBODIMENTS

According to a plurality of defects in the prior art, that it is impossible to achieve low temperature impact modifiers with good transparency and weatherability.

Subject of the recent invention is to provide a silicone-free impact modifier which has good weatherability, good transparency and good impact strength at low temperatures (<-50℃.). Surprisingly, it has been shown that by partial replacement of the monomers by a suitable plasticizer in the core, it is possible to reduce the glass transition temperature Tg of the impact modifiers based on acrylates, to maintain the transparency and weathering properties and thereby to increase the impact strength at low temperatures.

Examples of the monomers used are based on styrene and acrylic acid derivatives. Among the alkyl acrylates are the C1-C12 alkyl acrylates, e.g. Methyl acrylate, ethyl acrylate, butyl acrylate, 2-ethylhexyl acrylate, lauryl acrylate, are of particular importance. Suitable vinyl aromatic monomers are styrene and its mono- or polysubstituted derivatives, for example 4-methylstyrene, 4-ethylstyrene, 4-isopropylstyrene, 3,4-dimethylstyrene, 4-chlorostyrene, 4-bromostyrene, 3,4-dichlorostyrene. Styrene is particularly preferred. Other monomers can e.g. vinyl ethers such as vinyl isobutyl ether and vinyl esters such as vinyl acetate or vinyl propionate or C1-C8 alkyl methacrylates. The use of further monomers is not absolutely necessary to improve the impact resistance and transparency, but can be advantageous in some cases.

Crosslinking di- or polyunsaturated monomers are e.g. allyl, methallyl and vinyl esters of di-, tri- or higher carboxylic acids such as e.g. adipic acid divinyl ester, phthalic acid diallyl ester, maleic acid diallyl ester, fumaric acid diallyl ester; Allyl, methallyl and vinyl ethers of polyfunctional alcohols such as ethylene glycol divinyl ether, 1,3-butadiene diol divinyl ether, 1,4-butanediol divinyl ether, pentaerythritol triallyl ether; esters of acrylic or methacrylic acid with polyhydric alcohols such as ethylene glycol di (meth) acrylate, 1,2-propanediol di (meth) acrylate, 1,3-propanediol di (meth) acrylate, 1,3-butanediol di (meth) acrylate, 1,4 -Butanediol di (meth) acrylate, oligo- or polyethylene glycol di (meth) acrylate, divinylbenzene or mixtures of the substances mentioned. Di-unsaturated monomers, in particular divinylbenzene and 1,3-butanediol di (meth) acrylate and 1,4-butanediol di (meth) acrylate, are preferred. In addition to non-conjugated di- or polyunsaturated monomers, conjugated di- or polyunsaturated monomers can also be used. Diunsaturated monomers, in particular butadiene and isoprene, are also preferred here.

Typical plasticizers are based on azelates, alkylsulfonic acid phenyl esters, azelates, benzoates, chlorinated paraffins, citrates, epoxides, ricinolates, phosphates, valerates, phthalates, sebacates, terephthalates and trimellitates. Plasticizers based on adipic acid, azelaic acid and sebacic acid are particularly preferred.

The graft copolymers are prepared by emulsion polymerization. Serve as emulsifiers e.g. sodium, potassium or ammonium salts of saturated or unsaturated C8-C20 fatty acids such as lauric acid, stearic acid, palmitic acid, oleic acid and others, C8-C20-alkylsulfonic acids, sulfuric acid-C8-C20-alkyl esters, alkylbenzenesulfonic acids, abiethic acid and their derivatives, sulfosuccinic acid alkyl Diphenyl ether sulfonic acids.

By selecting the type and amount of the emulsifier, the particle size of the emulsion can be adjusted in a known manner. It can be between 50 and 300 nm. It is preferably in the range from 70 to 250 nm, particularly preferably between 70 and 200 nm. Both the optical properties (transparency, opalescence) and the mechanical properties (impact strength) are influenced by the particle size.

Water-soluble, thermally decomposing initiators or redox systems can be used as initiators. Suitable thermally decomposing initiators are, for example, sodium, potassium or ammonium persulfate and water-soluble azo compounds such as the sodium salt of 4,4'-azobis (4,4'-cyanopentanoic acid). Examples of suitable redox systems are cumene hydroperoxide, diisopropylbenzene hydroperoxide, tert-butyl hydroperoxide, tert-butyl peracetate in combination with reducing agents such as sodium formaldehyde sulfoxylate or ascorbic acid in the presence of iron salts. The persulfates mentioned can also be used in combination with reducing agents such as sodium or potassium metabisulfite in redox systems.

The polymerization temperature is generally between 10 and 100℃, preferably 50 to 90℃.

The invention is illustrated in more detail by the examples below, but is not restricted thereto.

Example 1 (comparative example based on example 1 in EP 0527605)

Step 1: making the core

1550 g of deionized water are filled into a 5 L reactor which can be heated to temperature, with stirrer, reflux condenser, thermometer, dropping funnel and gas inlet tube and heated to 55℃. Nitrogen is introduced. A dilute solution of p-nitrophenol (PNP) is added (0.002% based on the amount of monomers). A dilute solution of tartaric acid is then added (0.02% based on the amount of monomers) and then 2.5 g of a dilute solution (25%) of sodium dodecyl sulfate (0.05% based on the amount of monomers).

The emulsified monomer mixture (EMG) is prepared in a beaker with a stirrer from 440 g of water, 10 mL of a dilute solution (25%) of sodium dodecyl sulfate, 1440 g of butyl acrylate and 10 g of allyl methacrylate.

200 g of the EMG are added to the reactor with stirring, followed by 0.25 g of tert-butyl hydroperoxide (BHP) and 1.5 g of sodium formaldehyde sulfoxilate (SFS) in 30 g of deionized water. The temperature curve is tracked. When the exothermic reaction ceases, stirring is continued for 15 min. The reactor is cooled to 53℃.

The 2nd amount of EMG is then added at 180 g, followed by 0.9 g BHP. The cycle “exothermic reaction-15 min stirring-cooling" is repeated.

Then the 3rd amount of EMG is added at 760 g, followed by 0.9 g BHP. The cycle “exothermic reaction — stirring for 15 minutes and cooling" to 57℃ is repeated.

Then the 4th amount of EMG is added at 760 g, followed by 0.2 g BHP. When the exothermic phase is complete, 10 is stirred and then 0.25 g BHP and 0.15 g NSF in 10 g deionized water are added. The mixture is stirred for one hour and then cooled to 53℃.

Step 2: making the shell

2 g of sodium dodeclysulfate and 45 g of deionized water are added to this emulsion in the reactor, which contains the crosslinked polybutyl acrylate. After a stirring time of 5 min, a mixture of 200 g of methyl methacrylate and 0.8 g of n-dodecylcaptan is added, followed by 135 g of deionized water. At 53℃, stirring is continued for 10 min. Then 0.25 g of SFS in 25 g of deionized water are added. After a stirring time of 5 minutes, 0.3 g of sodium persulfate in 30 g of deionized water are added. When the exothermic reaction is complete, 0.1 g of SFS and 0.1 g of sodium persulfate in 55 g of deionized water are added. The temperature is kept under stirring for 60 min. The reaction mixture is filtered and processed analogously to EP 0527605 to the dry end product.

The end product has:

- a diameter of 150 to 300 nm

- a glass transition temperature of -45℃.

Example 2 (according to the invention)

Step 1: making the core

1550 g of deionized water are filled into a 5 L reactor which can be heated to temperature, with stirrer, reflux condenser, thermometer, dropping funnel and gas inlet tube and heated to 55℃. Nitrogen is introduced. A dilute solution of p-nitrophenol (PNP) is added (0.002% based on the amount of monomers). A dilute solution of tartaric acid is then added (0.02% based on the amount of monomers) and then 2.5 g of a dilute solution (25%) of sodium dodecyl sulfate (0.05% based on the amount of monomers).

The emulsified monomer mixture (EMG) is prepared in a beaker with a stirrer from 440 g of water, 10 ml of a dilute solution (25%) of sodium dodecyl sulfate, 360 g of di-i-nonyl adipate, 1080 g of butyl acrylate and 10 g of allyl methacrylate.

200 g of the EMG are added to the reactor with stirring, followed by 0.25 g of tert-butyl hydroperoxide (BHP) and 1.5 g of sodium formaldehyde sulfoxilate (SFS) in 30 g of deionized water. The temperature curve is tracked. When the exothermic reaction ceases, stirring is continued for 15 min. The reactor is cooled to 53℃.

The 2nd amount of EMG is then added at 180 g, followed by 0.9 g BHP. The cycle “exothermic reaction-15 min stirring-cooling" is repeated.

Then the 3rd amount of EMG is added at 760 g, followed by 0.9 g BHP. The cycle “exothermic reaction — stirring for 15 minutes and cooling" to 57℃ is repeated.

Then the 4th amount of EMG is added at 760 g, followed by 0.2 g BHP. When the exothermic phase is complete, 10 is stirred and then 0.25 g BHP and 0.15 g NSF in 10 g deionized water are added. The mixture is stirred for one hour and then cooled to 53℃.

Step 2: making the shell

2 g of sodium dodeclysulfate and 45 g of deionized water are added to this emulsion in the reactor, which contains the crosslinked polybutyl acrylate. After a stirring time of 5 min, a mixture of 200 g of methyl methacrylate and 0.8 g of n-dodecylcaptan is added, followed by 135 g of deionized water. At 53℃, stirring is continued for 10 min. Then 0.25 g of SFS in 25 g of deionized water are added. After a stirring time of 5 minutes, 0.3 g of sodium persulfate in 30 g of deionized water are added. When the exothermic reaction is complete, 0.1 g of SFS and 0.1 g of sodium

persulfate in 55 g of deionized water are added. The temperature is kept under stirring for 60 min. The reaction mixture is filtered and processed analogously to EP 0527605 to the dry end product.

The end product has:

a diameter of 150 to 300 nm

A glass transition temperature of -55℃

The present invention provides a graft copolymer with core-shell structure, characterized in that the core is produced by several steps of a successive emulsion polymerization of one or more monomers in the presence of one or more plasticizers, the plasticizer content being 10 to 80% and the monomer content being 90 to 10%.

Further, the monomers are selected from the group C1-C12-alkyl acrylates, C1-C12-alkyl methacrylates, styrene and its substituted derivatives as well as vinyl ethers, vinyl esters or vinyl propionate.

Further, the plasticizers are selected from the group consisting of azelate, phenyl alkylsulfonic acid, azelates, benzoates, chlorinated paraffins, citrates, epoxies, ricinolates, phosphates, valerates, phthalates, sebacates, terephthalates and trimellitates.

Further, the plasticizers are selected from the group dibutyl adipate, di (2-ethylhexyl) adipate, di-decyl adipate, di-i-nonyl adipate, di-i-octyl adipate, di-i-tridecyl adipate, Di-n-octyl adipate, dibutylazelate, di (2-ethylhexyl) azelate, di-decylazelate, di-i-nonylazelate, di-i-octylazelate, di-i-tridecylazelate, di-n-octylazelate, dibutyl sebazate, di (2- ethylhexyl) sebazate, di-decyl sebazate, di-i-nonyl sebazate, di-i-octyl sebazate, di-i-tridecyl sebazate and di-n-octyl sebazate.

The present invention also provides a process for the preparation of the graft copolymers, including:

a. Forming a latex from rubber-like polymer particles with a glass transition temperature Tg <-20℃ and a particle size of 50 to 300 nm in diameter is formed by emulsion polymerization

b. Forming, by sequential emulsion polymerization in the presence of the rubber-like polymer particle latex under conditions where substantially no new polymer particles are formed, a polymeric latex of the first core / intermediate shell, the intermediate polymer shell has

a. a glass transition temperature Tg> 50℃,

b. are predominantly formed from units derived from methyl methacrylate, and

c. about 5% to about 20% by weight of the first core / intermediate shell polymer particles;

c. Agglomerating the latex of the polymer particles of the first core / intermediate sheath to form a latex of the agglomerated particles with a diameter of at least 150 nm, the solids content of the latex of the polymer particles of the first core / intermediate sheath being not higher than 40% and the solids content not higher than 30%;

d. Forming a hard polymer encapsulation shell having a glass transition temperature of at least 60℃ in a final core / shell polymer by sequential emulsion polymerization on the agglomerated particles under conditions where essentially no new polymer particles are formed, the encapsulation shell

  a. are predominantly formed from units derived from methyl methacrylate

  b. 5 to 20% by weight of the final core-shell polymer, the total shell content being not less than 14% by weight of the final core-shell polymer, the sequential emulsion polymerization being carried out in the latex of the agglomerated particles and the final Core-shell polymer remain in latex form; and, if desired,

e. isolating the final core-shell polymer.

Further in the method, the final core-shell polymer is isolated by (a) spray drying or (b) coagulating, preferably by adding an aqueous solution of an inorganic acid salt.

The present invention further provides a process for producing a thermoplastic resin comprising:

a. Forming a final core-shell polymer by the method of any one of claims 1 to 6; and

b. Mixing, for example in an extruder or on a heated multi-roll mill, the final core-shell polymer with a thermoplastic resin under heat and shear conditions sufficient to cause the final core-shell polymer to be dispersed in particle domains equivalent in size the core / intermediate shell polymer or polymer particles prior to agglomeration; and

c. optionally processing the pre-stressed thermoplastic resin into an article by extrusion, calendering or injection molding.

Further in the method of process for producing a thermoplastic resin, the thermoplastic resin is a homo- or copolymer of vinyl chloride, a chlorinated PVC or a homo- or copolymer of methyl methacrylate or a technical resin such as a polyester of terephthalic acid and an aliphatic glycol, a polyamide, a polycarbonate B. a polyglutarimide, an acrylonitrile-butadiene-styrene resin or a mixture of at least two such resins.

In addition, the present invention provides a mixture comprising 60 to 99% by weight of a thermoplastic polymer and 1 to 40% by weight of the core-shell graft copolymer or produced by a process.

The mixture further contains one or more constituents: lubricant, processing aid, rheology modifier, dye, pigment, flame retardant, heat stabilizer, antioxidant, antiozonant, ultraviolet stabilizer, mold release agent, reinforcing or non-reinforcing filler.

Comparing to the prior art, the disclosure provides a graft copolymer with core-shell structure, the core is produced by several steps of a successive emulsion polymerization of one or more monomers in the presence of one or more plasticizers, the plasticizer content is 10 to 80% and the monomer content is 90 to 10%. If the plasticiser content is <10%, the graft copolymer shows no or a very minor effect to decrease the glass transition temperature. If the plasticiser content is >80%, the graft copolymer is impossible to graft the shell on the surface of the rubbery core. If the monomer content is >90%, the graft copolymer shows no or a very minor effect to decrease the glass transition temperature. If the monomer content is <10%, the graft copolymer is impossible to graft the shell on the surface of the rubbery core. The graft copolymer with core-shell structure ensures impact modifiers for low temperature applications with good transparency and weatherability.

According to process for the preparation of graft copolymers, the particle size of a nonmelting additive in PVC always has an influence on its performance. A particle too small or too large may not induce the optimum impact strength. An optimum impact resistance when the modifier has a particle size of about 200 nm. The 200 nm size seems to comprise the borderlines between various mechanisms that are happening during impact. Meanwhile, at a lower particle size (< 200 nm) crazing dominates the energy absorption.

The mixture comprises 60 to 99% by weight of a thermoplastic polymer and 1 to 40% by weight of the core-shell graft copolyme. The addition level of impact modifiers influences several parameters. A small increase in Charpy and Izod impacts strengths at low dosages. A rapid increase in Charpy and Izod impacts strengths at slightly higher dosages. Again a small improvement of impact strengths when the amount of modifier is further increased,a decrease in impact strength at high dosages, a decrease in tensile strength with increasing modifier load, an increase in both melt viscosity and cost with increasing amounts of impact modifier.

The minimum dosage of modifier should be 1% to see an increase of impact strength and that 40% is the point when impact strength may drop again. According to this the thermoplastic resin must vary in a range from 60 to 99%.

CLAIMS

1. Graft copolymer with core-shell structure, characterized in that the core is produced by several steps of a successive emulsion polymerization of one or more monomers in the presence of one or more plasticizers, the plasticizer content being 10 to 80% and the monomer content being 90 to 10%.
2. Graft copolymer according to claim 1, characterized in that the monomers are selected from the group C1-C12-alkyl acrylates, C1-C12-alkyl methacrylates, styrene and its substituted derivatives as well as vinyl ethers, vinyl esters or vinyl propionate.
3. Graft copolymer according to one of the preceding claims, characterized in that the plasticizers are selected from the group consisting of azelate, phenyl alkylsulfonic acid, azelates, benzoates, chlorinated paraffins, citrates, epoxies, ricinolates, phosphates, valerates, phthalates, sebacates, terephthalates and trimellitates.
4. Graft copolymer according to one of the preceding claims, characterized in that the plasticizers are selected from the group dibutyl adipate, di (2-ethylhexyl) adipate, di-decyl adipate, di-i-nonyl adipate, di-i-octyl adipate, di-i-tridecyl adipate, Di-n-octyl adipate, dibutylazelate, di (2-ethylhexyl) azelate, di-decylazelate, di-i-nonylazelate, di-i-octylazelate, di-i-tridecylazelate, di-n-octylazelate, dibutyl sebazate, di (2- ethylhexyl) sebazate, di-decyl sebazate, di-i-nonyl sebazate, di-i-octyl sebazate, di-i-tridecyl sebazate and di-n-octyl sebazate.
5. Process for the preparation of graft copolymers according to claims 1 to 4, characterized in that
    a. Forming a latex from rubber-like polymer particles with a glass transition temperature Tg <-20℃ and a particle size of 50 to 300 nm in diameter is formed by emulsion polymerization;
    b. Forming, by sequential emulsion polymerization in the presence of the rubber-like polymer particle latex under conditions where substantially no new polymer particles are formed, a polymeric latex of the first core / intermediate shell, the intermediate polymer shell has
        a. a glass transition temperature Tg> 50℃,
        b. are predominantly formed from units derived from methyl methacrylate, and
        c. about 5% to about 20% by weight of the first core / intermediate shell polymer particles;
    c. Agglomerating the latex of the polymer particles of the first core / intermediate sheath to form a latex of the agglomerated particles with a diameter of at least 150 nm, the solids content of the latex of the polymer particles of the first core / intermediate sheath being not higher than 40% and the solids content not higher than Is 30%;
    d. Forming a hard polymer encapsulation shell having a glass transition temperature of at least 60℃ in a final core / shell polymer by sequential emulsion polymerization on the

agglomerated particles under conditions where essentially no new polymer particles are formed, the encapsulation shell

   a. are predominantly formed from units derived from methyl methacrylate
   b. 5 to 20% by weight of the final core-shell polymer, the total shell content being not less than 14% by weight of the final core-shell polymer, the sequential emulsion polymerization being carried out in the latex of the agglomerated particles and the final Core-shell polymer remain in latex form; and, if desired,

e. isolating the final core-shell polymer.

6. Method according claim 5, wherein the final core-shell polymer is isolated by (a) spray drying or (b) coagulating, preferably by adding an aqueous solution of an inorganic acid salt.
7. A process for producing a thermoplastic resin comprising:
   a. Forming a final core-shell polymer by the method of any one of claims 1 to 6; and
   b. Mixing, for example in an extruder or on a heated multi-roll mill, the final core-shell polymer with a thermoplastic resin under heat and shear conditions sufficient to cause the final core-shell polymer to be dispersed in particle domains equivalent in size the core / intermediate shell polymer or polymer particles prior to agglomeration; and
   c. optionally processing the pre-stressed thermoplastic resin into an article by extrusion, calendering or injection molding.
8. Method according to claim 7, wherein the thermoplastic resin is a homo- or copolymer of vinyl chloride, a chlorinated PVC or a homo- or copolymer of methyl methacrylate or a technical resin such as a polyester of terephthalic acid and an aliphatic glycol, a polyamide, a polycarbonate B, a polyglutarimide, an acrylonitrile-butadiene-styrene resin or a mixture of at least two such resins.
9. Mixture comprising 60 to 99% by weight of a thermoplastic polymer and 1 to 40% by weight of the core-shell graft copolymer according to one of Claims 1 to 4 or produced by a process according to one of Claims 5 to 6.
10. Mixture according to claim 9, which further contains one or more constituents: lubricant, processing aid, rheology modifier, dye, pigment, flame retardant, heat stabilizer, antioxidant, antiozonant, ultraviolet stabilizer, mold release agent, reinforcing or non-reinforcing filler.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN2020/093801

A. CLASSIFICATION OF SUBJECT MATTER

C08J 3/12(2006.01)i; C09D 151/00(2006.01)i; C08F 285/00(2006.01)i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C08J3/-; C09D151/-; C08F285/-

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)

WPI,EPODOC,CNPAT,CNKI:shell, sequential+, copolymer, core, shell, polymer+, graft,emulsion, plasticizer+, plasticiser

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2018319918 A1 (AGC INC.) 08 November 2018 (2018-11-08) description, paragraphs [0013], [0018], [0100], [0103]-[0111], [0183]-[0186], [0218]	1-10
A	WO 2015024882 A1 (BASF SE.) 26 February 2015 (2015-02-26) claims 1-17	1-10
A	CN 110872397 A (FUJI XEROX CO. LTD.) 10 March 2020 (2020-03-10) description, paragraphs [0005]-[0110]	1-10
A	WO 2007055550 A1 (KOLON INC. et al.) 18 May 2007 (2007-05-18) description, pages 3-11	1-10

☐ Further documents are listed in the continuation of Box C. ☑ See patent family annex.

* Special categories of cited documents:

“A” document defining the general state of the art which is not considered to be of particular relevance

“E” earlier application or patent but published on or after the international filing date

“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)

“O” document referring to an oral disclosure, use, exhibition or other means

“P” document published prior to the international filing date but later than the priority date claimed

“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

“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

“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

“&” document member of the same patent family

Date of the actual completion of the international search **11 August 2020**	Date of mailing of the international search report **27 August 2020**
Name and mailing address of the ISA/CN **National Intellectual Property Administration, PRC** **6, Xitucheng Rd., Jimen Bridge, Haidian District, Beijing 100088** **China** Facsimile No. **(86-10)62019451**	Authorized officer **MA,Hua** Telephone No. **86-（10）-53962179**

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
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