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(54) Title: STABLE POLYMER COMPOSITES

(57) Abstract: The present invention refers to a polymeric composite, a process for preparing said polymeric composite, a polymeric composite obtainable by said process and the use of stabilizers in vinyl polymers.



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STABLE POLYMER COMPOSITES

FIELD OF THE INVENTION

5 The present invention relates to the stabilization of vinyl polymers. More specifically, the present invention relates to a polymeric composite, a process for preparing said polymeric composite and the use of stabilizers for vinyl polymers.

BACKGROUND

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Polymers suffer degradation processes during their life-cycle which affect their appearance, color and mechanical properties such as strength and malleability. In particular, polymers react with atmospheric oxygen through autoxidation processes through mechanisms that depend on the polymer structure and external conditions that
15 are essentially temperature and light exposure.

15

Polymers are commonly protected by adding stabilizers into their composition. Most of the stabilizers are incorporated during the polymer manufacture thus, being affected by evaporation losses. Most antioxidants and UV stabilizers act as radical scavengers
20 during polymer autoxidation delaying the degradation process or weathering. For instance, Chinese Patent Application No. CN105860131 (A) describes the application of graphene-based hybrid materials comprising nanomaterials such as calcium carbonate, titanium dioxide, barium sulfate, montmorillonite, ferric oxide and calcium carbonate to polymers as heat-resistant stabilizers. According to CN105860131 (A),
25 free radicals are stabilized through the electronic conjugation effect of the benzene ring structure of graphene and acids are absorbed by inorganic nanoparticles leading to the stabilization of the polymer under heat. However, stabilizers effectiveness is limited by their distribution and/or solubility in the polymer matrix. Additionally, stabilizer migration in the polymer can also reduce their activity. Also, polymer color and appearance can
30 be affected by the presence of stabilizers.

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Thermal stabilizers such as heavy metals derivatives are traditionally used in certain polymers since they for example minimize the loss of HCl in the degradation process of polyvinyl chloride (PVC). However, there are few documents describing antioxidant
35 effects of metals. For example, Lin D. G. et al. [Russian Journal of Applied Chemistry

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76 (2003) 827-830] describes that the stabilizing effect under thermal oxidation of polyethylene of an amide antioxidant is enhanced in the presence of dispersed copper particles. Also, Vodnik V.V. et al. [European Polymer Journal 46 (2010) 137–144] discloses that poly(methyl methacrylate) (PMMA) with silver nanoparticles dispersed in
5 said polymer shows a higher thermo-oxidative stability than PMMA. Nevertheless, the stabilizing mechanisms of metals in polymers and their effects is not well established and therefore, difficult to predict. These documents incorporate the metal particles to the polymer matrix increasing processing costs. In addition, the use of metal particles or nanoparticles lead to changes in the appearance of the final product such as
10 changes in color or texture.

In summary, there is a need to develop new polymer stabilizers that allow their post-processing incorporation to the polymer and that overcome prior art limitations such as evaporation losses, migration and undesired effects in polymer appearance.

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BRIEF DESCRIPTION OF THE INVENTION

The inventors of the present invention have found that transition metal Atomic Quantum Clusters (AQC)s are stabilizers for vinyl polymers in oxidation degradation
20 processes such as in those oxidation processes wherein vinyl polymers react with atmospheric oxygen through autoxidation process through mechanisms that depend on the vinyl polymer structure and external conditions like temperature and/or light exposure. The discovery of transition metal AQC)s as new vinyl polymer stabilizers represents a breakthrough since they allow post-production application to the vinyl
25 polymers, thus avoiding evaporation losses and migration. Additionally, they do not affect vinyl polymer appearance, color or texture. This approach is of great importance for a large variety of applications of vinyl polymers in various technological fields, since it solves the current limitations of the prior art.

30 Thus, in a first aspect, the invention is directed to a polymeric composite comprising:

- a vinyl polymeric substrate; and
- transition metal AQC)s comprising less than 200 zero-oxidation-state transition metal atoms;

wherein said transition metal AQC)s are coating said vinyl polymeric substrate;

35 wherein the transition metal AQC)s are coating said vinyl polymeric substrate in a

concentration of less than 0.10 μg per square centimeter;
wherein the metal of the transition metal AQC is selected from Au, Ag, Co, Cu, Pt, Fe, Ni or their bi-metal and multi-metal combinations; and
wherein transition metal AQC has a mean size of less than 2 nm.

5

In a second aspect, the invention is directed to a process for preparing a polymeric composite comprising the following step:

- coating a vinyl polymeric substrate with a composition comprising transition metal AQC comprising less than 200 zero-oxidation-state transition metal atoms; wherein the transition metal AQC is coating said vinyl polymeric substrate in a concentration of less than 0.10 μg per square centimeter; wherein the metal of the transition metal AQC is selected from Au, Ag, Co, Cu, Pt, Fe, Ni or their bi-metal and multi-metal combinations; and wherein transition metal AQC has a mean size of less than 2 nm.

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In a third aspect, the present invention is directed to a polymeric composite obtainable by the process of the present invention.

In a further aspect, the present invention is directed to the use of transition metal AQC as stabilizers in vinyl polymers against the degradation of said vinyl polymers by oxidation processes.

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FIGURES

25 Figure 1 (a) ATR-FTIR spectra of a pristine polyisoprene (PI) film (a') and of a PI film coated with 0.02 μg of Ag_5 AQC per squared cm (b') after 50 h of accelerated photoageing; and (b) normalized intensity values of the carbonyl ATR-FTIR band against the absorption ascribed to C-H deformation vibration band for the pristine PI film (a') and for the PI film coated Ag_5 AQC (b') oxidation over standard accelerated photoageing
30 time (h).

DETAILED DESCRIPTION OF THE INVENTION

Unless defined otherwise, all technical and scientific terms used herein have the same
35 meaning as commonly understood to one of ordinary skill in the art to which this

disclosure belongs. As used herein, the singular forms “a” “an” and “the” include plural reference unless the context clearly dictates otherwise.

Polymeric composite

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In a first aspect, the invention is directed to a polymeric composite comprising:

- a vinyl polymeric substrate; and
- transition metal AQC's comprising less than 200 zero-oxidation-state transition metal atoms;

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wherein said transition metal AQC's are coating said vinyl polymeric substrate; wherein the transition metal AQC's are coating said vinyl polymeric substrate in a concentration of less than 0.10 μg per square centimeter;

wherein the metal of the transition metal AQC's is selected from Au, Ag, Co, Cu, Pt, Fe, Ni or their bi-metal an multi-metal combinations; and

15

wherein transition metal AQC's have a mean size of less than 2 nm.

In a particular embodiment, the polymeric composite further comprises more layers; wherein said layers are on top of the transition metal AQC's comprising less than 200 metal atoms coating said vinyl polymeric substrate or below said vinyl polymeric substrate; preferably below said vinyl polymeric substrate. In a more particular embodiment, said layers are of organic or inorganic materials; preferably of organic materials; more preferably of polymeric materials.

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In a more particular embodiment, the polymeric composite of the present invention is a vinyl polymeric composite.

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Vinyl polymeric substrate

The expression “vinyl polymeric substrate” refers to substrate comprising a vinyl polymer or copolymer; preferably a vinyl polymer. The vinyl polymeric substrate of the present invention may further comprise one or more layers; wherein the top layer consists of a vinyl polymer. The further layers below the vinyl polymer layer of the vinyl polymeric substrate may be of different materials; preferably of different polymeric materials; more preferably of different vinyl polymeric materials.

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In the context of the present invention, the term “polymeric composite” relates to a material comprising at least two constituent materials, at least a vinyl polymeric substrate and transition metal AQC comprising less than 200 metal atoms. In a particular embodiment, the polymeric composite consists of a vinyl polymeric substrate and transition metal AQC comprising less than 200 metal atoms.

The vinyl polymeric substrate degrades through a radical degradation mechanism known in the art such as an oxidation process; in particular is related to a radical degradation mechanism. Non-limiting examples of vinyl polymeric substrates suitable for the present invention are vinyl polymers or copolymers; preferably vinyl polymers.

In a preferred embodiment the “vinyl polymeric substrate” of the present invention consists of a vinyl polymer or copolymer; preferably a vinyl polymer.

In a more preferred embodiment the “vinyl polymeric substrate” of the present invention consists of one layer; preferably one layer of a vinyl polymer; more preferably a thin film layer of a vinyl polymer.

A vinyl polymer or copolymer is a polymer or copolymer derived from vinyl monomers known in the art. Said vinyl monomers may be unsubstituted or substituted once or more times, and wherein each substituent is independently selected from alkyl, aryl, halogen, ester, amide, carboxylic acid, -OH and -CN. “Alkyl” refers to a straight or branched hydrocarbon chain radical consisting of 1 to 6 carbon atoms, containing no unsaturation, and which is attached to the rest of the monomer by a single bond, e.g., methyl, ethyl, or propyl, preferably methyl. “Aryl” refers to single and double aromatic ring radicals containing from 6 to 10 carbon ring atoms, such as phenyl or naphthyl, preferably phenyl. “Halogen” refers to bromo, chloro, iodo or fluoro, preferably chloro. “Ester” is an -OC(O)R group, wherein R is alkyl as previously defined. “Amide” is an -NC(O)R group, wherein R is alkyl as previously defined. “Carboxylic acid” is a -COOH group and may be protonated or deprotonated.

In a particular embodiment, the vinyl polymer of the vinyl polymeric substrate of the present invention is selected from the group consisting of polyethylene, polypropylene, polyisoprene (PI), polybutadiene, polystyrene, polyvinyl chloride (PVC), polyvinyl acetate (PVAc), polyvinyl alcohol (PVA), polyacrylate,

polymethacrylate, polyacrylonitrile, polyvinylidene chloride polyvinylpyrrolidone, derivatives and/or combinations thereof.

In another particular embodiment, the vinyl polymer of the vinyl polymeric substrate of the present invention is selected from the group consisting of polyethylene, polypropylene, polyisoprene (PI), polybutadiene, polyvinyl chloride (PVC), polyvinyl acetate (PVAc), polyvinyl alcohol (PVA), polyacrylate, polymethacrylate, polyacrylonitrile, polyvinylidene chloride polyvinylpyrrolidone, derivatives and/or combinations thereof.

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In a more particular embodiment, the vinyl polymer of the vinyl polymeric substrate of the present invention is selected from the group consisting of polyethylene, polypropylene, polyisoprene (PI), polybutadiene, polystyrene, polyvinyl chloride (PVC), polyvinyl acetate (PVAc), polyvinyl alcohol (PVA), polyacrylonitrile, polyvinylidene chloride, derivatives and/or combinations thereof.

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In another particular embodiment, the copolymer of the vinyl polymeric substrate of the present invention comprises polyethylene, polypropylene, polyisoprene (PI), polybutadiene, polystyrene, polyvinyl chloride (PVC), polyvinyl acetate (PVAc), polyvinyl alcohol (PVA), polyacrylate, polymethacrylate, polyacrylonitrile, polyvinylidene chloride, or polyvinylpyrrolidone; and a repeating unit selected from the above mentioned vinyl monomers.

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In a more particular embodiment the vinyl polymeric substrate is a polyisoprene (PI) and its derivatives. In a more particular embodiment the vinyl polymeric substrate is a polyisoprene (PI) polymer or copolymer; preferably a polyisoprene (PI) polymer. In an embodiment, the copolymer comprises polyisoprene (PI) and a repeating unit selected from the above mentioned vinyl monomers.

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Non-limiting examples of polyisoprene polymers suitable for the vinyl polymeric substrate of the present invention are natural Gutta-percha, natural rubber, cis-1,4-polyisoprene, trans-1,4-polyisoprenes, derivatives and combinations thereof.

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In a particular embodiment, the vinyl polymeric substrate is a film, preferably a thin film; more preferably a film with a thickness of between 0.001 and 10000 mm;

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preferably a film with a thickness of between 0.01 and 1000 nm.

AQCs

5 In the context of the present invention, the expressions “Atomic Quantum Cluster” or “Atomic Quantum Clusters” are abbreviated as AQC and AQCs respectively. AQCs are known for not behaving like a “metal” but for having a molecular-like behavior. Therefore, new properties which are not observed in nanoparticles, microparticles or bulk metals appear in AQCs. Therefore, the physical-chemical properties of the AQC
10 cannot be simply extrapolated from those of the nano/microparticles.

Transition metal AQCs of the present invention comprise less than 200 metal atoms; preferably less than 200 zero-oxidation-state transition metal atoms, Mn, (Mn, $n < 200$). Preferably, transition metal AQCs of the present invention have a mean size of less
15 than 2 nm.

In a particular embodiment, transition metal AQCs of the present invention are further characterized by comprising less than 100 zero-oxidation-state transition metal atoms (Mn, $n < 100$); preferably less than 55 zero-oxidation-state transition metal atoms (Mn, $n < 55$); more preferably between 4 and 13 zero-oxidation-state transition metal atoms (Mn, $4 \leq n \leq 13$) and even more preferably 5 zero-oxidation-state transition metal atoms (Mn, $n = 5$).
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In a more particular embodiment, transition metal AQCs of the present invention may
25 be chemically functionalized, for example by organic ligands known in the art.

In a preferred embodiment, transition metal AQCs of the present invention consist of less than 200 zero-oxidation-state transition metal atoms, Mn, (Mn, $n < 200$); preferably less than 100 zero-oxidation-state transition metal atoms (Mn, $n < 100$); more preferably
30 less than 55 zero-oxidation-state transition metal atoms (Mn, $n < 55$); more preferably less than 34 zero-oxidation-state transition metal atoms (Mn, $n < 34$); even more preferably between 4 and 13 zero-oxidation-state transition metal atoms (Mn, $4 \leq n \leq 13$) and even more preferably 5 zero-oxidation-state transition metal atoms (Mn, $n = 5$).

In a preferred embodiment, transition metal AQC's of the present invention are monodispersed zero-valent transition metal AQC's consisting of less than 200 zero-oxidation-state transition metal atoms, Mn, (Mn, $n < 200$); preferably less than 100 zero-oxidation-state transition metal atoms (Mn, $n < 100$); more preferably less than 55 zero-oxidation-state transition metal atoms (Mn, $n < 55$); more preferably less than 34 zero-oxidation-state transition metal atoms (Mn, $n < 34$); preferably between 4 and 13 zero-oxidation-state transition metal atoms (Mn, $4 \leq n \leq 13$) and even more preferably 5 zero-oxidation-state transition metal atoms (Mn, $n = 5$).

10 In a more particular embodiment the transition metal AQC's of the present invention comprise 5, 18 or 34 zero-oxidation-state transition copper atoms, 2 or 3 zero-oxidation-state transition gold atoms or 2, 4 or 5 zero-oxidation-state transition silver atoms; preferably comprise 5 zero-oxidation-state transition copper atoms or 5 zero-oxidation-state transition silver atoms; more preferably comprise 5 zero-oxidation-state transition silver atoms.

In an even more particular embodiment, the transition metal AQC's of the present invention consist of 5, 18 or 34 zero-oxidation-state transition copper atoms, 2 or 3 zero-oxidation-state transition gold atoms or 2, 4 or 5 zero-oxidation-state transition silver atoms; preferably 2, 4 or 5 zero-oxidation-state transition silver atoms; preferably consist of 5 zero-oxidation-state transition copper atoms or 5 zero-oxidation-state transition silver atoms; more preferably consist of 5 zero-oxidation-state transition silver atoms.

25 The transition metal AQC's of the present invention are stable transition metal AQC's over time i.e.: they conserve the number metal atoms and their properties over the time. In the context of the present invention "stable transition metal AQC's" are understood as those comprising zero-oxidation-state transition metal groupings of atoms which conserve the number of atoms and, therefore, their properties, over time, so that they can be isolated and manipulated like any other chemical compound without changes in their properties over the time. In a particular embodiment, transition metal AQC's of the present invention are stable during a period of at least 10 hours; preferably at least 1 month; more preferably at least 1 year; even more preferably at least 5 years.

Suitable transition metal AQC's for the present invention include any transition metal AQC's comprising less than 200 transition metal atoms available in the market or obtained in the laboratory by methods known in the art. Preferably, transition metal AQC's used in the present invention are synthesized according to the process
5 described in patent ES2277531B2, and its corresponding WO 2007/017550 A1 and in documents N. Vilar-Vidal et al. [N. Vilar-Vidal et al. Small 2014, 10, No. 18, 3632–3636] and Huseyinova S. et al. [Huseyinova S. et al. J. Phys. Chem. C 2016, 120, 15902–15908]. The methods for obtaining transition metal AQC's described in said documents are based on the reduction of a transition metal salt or transition metal ion
10 while maintaining a kinetic control for a slow reduction and a low concentration of reagents in the reaction medium. Thus, the clustering formation is not limited to the type of synthesis, or the specific transition metallic element disclosed in said documents. Any other reduction of a transition metal salt in solution can be used for the production of the transition metal AQC's of the present invention, provided the reaction
15 being slow enough to observe the evolution of the transition metal AQC's and stop it (e.g. by cooling, dilution and/or fixation/separation of the clusters of the reaction medium) to obtain transition metal AQC's of a specific size as known in the art.

In a preferred embodiment, transition metal AQC's of the present invention are
20 understood as formed exclusively by zero-oxidation-state (i.e. zero-valent) transition metal atoms, Mn, stable over time, with less than 200 metal atoms (Mn, $n < 200$) and with a mean size of less than 2 nm.

The metals of the transition metal AQC's of the present invention are transition metals;
25 preferably said transition metals are selected from Au, Ag, Co, Cu, Pt, Fe, Pd, Ni or their bi-metal and multi-metal combinations; more preferably the transition metals are selected from Au, Ag, Cu, Pd or their bi-metal and multi-metal combinations; even more preferably are selected from Au, Ag, Cu and their combination thereof. In a particular embodiment, the metal of the transition metal AQC's of the present invention
30 are Ag or Cu; preferably Ag.

In a preferred embodiment, transition metal AQC's of the present invention comprise
less than 34 zero-oxidation-state transition metal atoms; wherein said zero-oxidation-state transition metal atoms are selected from Au, Ag or Cu; preferably Ag or Cu; more
35 preferably Ag.

In a preferred embodiment, the transition metal AQC of the present invention consists of zero-oxidation-state atoms of Ag, Cu or a combination thereof; preferably of zero-oxidation-state atoms of Ag.

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In a more preferred embodiment, transition metal AQC of the present invention consists of less than 34 zero-oxidation-state transition metal atoms; wherein said zero-oxidation-state transition metal atoms are selected from Au, Ag or Cu; preferably Ag or Cu; more preferably Ag; preferably of less than 13 zero-oxidation-state transition metal

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In a more preferred embodiment, the transition metal AQC of the present invention consists of less than 200 zero-oxidation-state Ag atoms; preferably of less than 100 zero-oxidation-state Ag atoms; more preferably of less than 55 zero-oxidation-state Ag

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atoms; even more preferably of between 4 and 13 zero-oxidation-state Ag atoms and even much more preferably of 5 zero-oxidation-state Ag atoms.

In a particular embodiment, the transition metal AQC is a 5 atoms zero-valent silver metal cluster Ag_5 .

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In a more preferred embodiment, the transition metal AQC of the present invention consists of less than 200 zero-oxidation-state Cu atoms; preferably of less than 100 zero-oxidation-state Cu atoms; more preferably of less than 55 zero-oxidation-state Cu atoms; even more preferably of between 4 and 13 zero-oxidation-state Cu atoms and

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even much more preferably of 5 zero-oxidation-state Cu atoms.

In a preferred embodiment, the transition metal AQC of the present invention are monodispersed transition metal AQC. In the context of the present invention, the term "monodispersed" refers to transition metal AQC of uniform size and dispersed

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(opposed to being agglomerated or aggregated) as known in the art.

In one embodiment, the mean size of the transition metal AQC of the present invention is less than 1.2 nm. In a particular embodiment, the mean size of the transition metal AQC of the present invention is between 0.3 nm and 1.2 nm. In a

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invention is between 0.3 nm and 0.9 nm, preferably between 0.3 nm and 0.5 nm. In the context of the present invention, the transition metal AQC's "mean size" can be measured by techniques known in the art such as high-resolution scanning-transmission electron microscope (HR-STEM). For example, the mean size of the transition metal AQC's of the present invention may be calculated as the arithmetic mean size (understood as arithmetic mean diameter) calculated from a statistically significant number of size measures (over 50 or over 100) of transition metal AQC's obtained from high-resolution scanning-transmission electron microscope (HR-STEM) techniques as known in the art.

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In the context of the present invention, the term "coating" refers to the transition metal AQC's of the present invention being on the surface of the vinyl polymeric substrate of the present invention. The transition metal AQC's of the present invention may be covering the surface of the vinyl polymeric substrate as a thin film, forming aggregates or agglomerates of transition metal AQC's or as individual transition metal AQC's; preferably as aggregates or agglomerates of transition metal AQC's or as individual transition metal AQC's; more preferably as individual transition metal AQC's. Said coating may be an all-over coating covering all the substrate surfaces or it may only cover parts of the substrate surfaces (partial coating). In addition, said coating may be continuous or discontinuous; preferably discontinuous. Said coating can also be addressed as coating layers.

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In a particular embodiment, the polymeric composite of the present invention comprises transition metal AQC's coating said vinyl polymeric substrate in a concentration of less than 0.10 μg per square centimeter; particularly of less than 0.08 μg per square centimeter; more particularly of less than 0.06 μg per square centimeter; preferably of less than 0.05 μg per square centimeter; more preferably of less than 0.04 μg per square centimeter; even more preferably of about 0.02 μg per square centimeter. In a preferred embodiment the transition metal AQC's coating the vinyl polymeric substrate are homogeneously dispersed on the surface of said vinyl substrate.

30

In another particular embodiment, the polymeric composite of the present invention comprises transition metal AQC's coating the vinyl polymeric substrate in a

concentration of less than 0.10 ng per square meter; preferably of less than 0.05 ng per square meter; more preferably of less than 0.02 ng per square meter.

The vinyl polymeric substrate of the present invention can be optionally treated under
5 different mechanization processes to generate different morphologies. In an embodiment, is the vinyl polymeric substrate of the present invention in the form of films or aggregated, pelletized, cylindrical, discoidal, spherical, tabular, ellipsoidal, cubic, acicular, flakey, angular, equant or forming irregular shapes; preferably in the form of films; more preferably in the form of thin films with a thickness below 1000
10 microns; preferably below 100 microns; more preferably below 10 microns.

Transition metal AQC's may be used as stabilizers for the polymeric composite of the present invention alone or in combination with other stabilizer or mixtures of stabilizers known in the art. In an embodiment, the vinyl polymeric substrate of the present
15 invention comprises further stabilizers in its composition. Non-limiting examples of stabilizers known in the art are antioxidants such as radical scavengers, hydroperoxides scavengers, or antiozonants; light stabilizers such as UV absorbers, quenchers, or amine light stabilizers; acid scavengers; heat stabilizers; flame retardants; biocides and combination thereof. In a particular embodiment, the polymeric composite of the
20 present invention further comprises a stabilizer different from the transition metal AQC's of the present invention; preferably a light stabilizer; more preferably hindered amine light stabilizer (HALS) as known in the art; even more preferably a 2,2,6,6-tetramethyl-piperidine derivative.

25 In a preferred embodiment, the polymeric composite of the present invention comprises:

- a polyisoprene substrate; and
- transition metal AQC's consisting of 5 zero-valent silver metal atoms;

wherein said transition metal AQC's consisting of 5 zero-valent silver metal atoms are
30 coating the surface of said a polyisoprene substrate in a concentration of below 0.05 µg per square cm; preferably in a concentration of about 0.02 µg per square cm.

The authors of the present invention have surprisingly observed that by coating a vinyl polymeric substrate with transition metal AQC's comprising less than 200 metal atoms
35 as defined above, said vinyl polymeric substrate is stabilized. In particular, the vinyl

polymeric substrate is oxidized in less extent and at a reduced rate under accelerated photoageing conditions when is coated with said transition metal AQC. Without being bound to any theory in particular the inventors believe that transition metal AQC comprising less than 200 metal atoms affect the vinyl polymeric substrate degradation
5 through an oxidation catalytic mechanism different from those reported for traditional stabilizers, enhancing the oxidation through a pathway that leads to the formation of hydroxyl groups (-OH) in the vinyl polymer instead of unstable carbonyl groups and therefore, yielding stable products. In the present invention, the presence and/or concentration of hydroxyl groups or carboxyl groups on the surface of the vinyl
10 polymeric substrate are measured by ATR-FTIR techniques known in the art to estimate the extent of oxidation suffered by the polymeric composite or by the vinyl polymeric substrate.

In addition, the post-processing addition of AQC to the polymeric substrate has
15 advantages over synthesized the AQC *"in situ"* during polymerization leading to higher stabilization of the polymeric substrate and reduced or absence of migration of the AQC in the polymer.

Surprisingly, it has been observed that the transition metal AQC coating the vinyl
20 polymeric substrate of the present invention do not change the color or the appearance of the vinyl polymeric substrate.

In a first aspect, the invention is directed to a polymeric composite consisting of:

- the vinyl polymeric substrate described above in any of its particular
25 embodiments; and
- the transition metal AQC comprising less than 200 metal atoms in any of its particular embodiments;

wherein said transition metal AQC are coating said vinyl polymeric substrate.

30 Process for the preparation of a polymeric composite

In a second aspect, the invention is directed to a process for preparing the polymeric composite of the present invention comprising the following step:

- coating a vinyl polymeric substrate with a composition comprising transition
35 metal AQC comprising less than 200 zero-oxidation-state transition metal

atoms;

wherein the transition metal AQC's are coating said vinyl polymeric substrate in a concentration of less than 0.10 μg per square centimeter;

wherein the metal of the transition metal AQC's is selected from Au, Ag, Co, Cu, Pt, Fe, Ni or their bi-metal and multi-metal combinations; and

wherein transition metal AQC's have a mean size of less than 2 nm.

The composition comprising transition metal AQC's comprising less than 200 metal atoms is referred herein as the composition of the present invention or just composition.

In a particular embodiment, the coating step of the process of the present invention further comprises applying one or more layers of coatings with a composition comprising transition metal AQC's comprising less than 200 metal atoms in one or more additional coating steps.

In a particular embodiment, the coating step of the process of the present invention may be performed by dip coating, spray coating, vapor deposition or brush coating techniques; preferably by spray coating techniques; more preferably by using an aerograph. In a more particular embodiment, one or more coating or coating layers are formed comprising a composition comprising transition metal AQC's comprising less than 200 metal atoms; preferably one or more coating or coating layers are formed consisting of a composition comprising transition metal AQC's comprising less than 200 metal atoms.

In a preferred embodiment, the process for preparing the polymeric composite of the present invention comprises the following steps:

a) providing:

a. a vinyl polymeric substrate; and

b. a composition comprising metal AQC's comprising less than 200 metal atoms; and

b) coating said vinyl polymeric substrate with said composition comprising metal AQC's comprising less than 200 metal atoms.

In a more particular embodiment, the coating step (b) of the process of the present

invention as described above is performed by spraying the composition comprising metal AQC's comprising less than 200 metal atoms, to the surface of the vinyl polymeric substrate.

5 In an even more particular embodiment, the process for preparing the polymeric composite of the present invention further comprises a step c) of :

c) drying the vinyl polymeric substrate of step (b); preferably drying the surface of the vinyl polymeric substrate; more preferably drying the surface of the vinyl polymeric substrate at room temperature.

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In a particular embodiment, the composition of the present invention may further comprise a solvent. In a preferred embodiment, the solvent is a polar solvent; preferably water. In another preferred embodiment, the transition metal AQC's are in the composition of the present invention in a concentration below 100 mg/L; 15 preferably between 1 and 100 mg/L, more preferably between 40 and 90 mg/L, even more preferably of 80 mg/L. Moreover, the concentrations of the transition metal AQC's of the present invention in the composition may be measured by UV-VIS spectroscopy. Suitable compositions of transition metal AQC's may be those available in the market or obtained in the laboratory by methods known in the art such as those described 20 above. Transition metal AQC's may be dispersed in said solvent by methods known in the art to allow their subsequent application to the surface of the vinyl polymeric substrate. In an embodiment, transition metal AQC's are homogeneously dispersed in the composition of the present invention. In an embodiment, the composition may further comprise other compounds such as dispersants or polymer stabilizers as 25 known in the art. Therefore, the coating, coating layer or coating layers of the present invention may further comprise other compounds such as dispersant, fillers and/or polymer stabilizers; preferably polymer stabilizers.

In a particular embodiment, the composition of the present invention consist of the 30 transition metal AQC's of the present invention, and a solvent; preferably water. In a preferred embodiment, the composition of the present invention consist of (a) transition metal AQC's consisting of 5 zero-valent silver metal atoms and (b) water.

In a more particular embodiment, the spraying step of the present invention is 35 performed by spraying systems known in the art. Non-limiting examples of spraying

systems are aerographs and nebulization systems known in the art.

In a preferred embodiment, the process for preparing the polymeric composite of the present invention comprises the following steps:

- 5 – coating a vinyl polymeric substrate with the transition metal AQC of the present invention;
- wherein the coating step of the process of the present invention comprises:
- a) providing a composition consisting of the transition metal AQC of the present invention in a solvent and a vinyl polymeric substrate;
- 10 b) applying said composition to the surface of the vinyl polymeric substrate; and
- drying the vinyl polymeric substrate of step (b) at room temperature.

In a preferred embodiment, the process for preparing the polymeric composite of the present invention comprises the following steps:

- 15 – coating a vinyl polymeric substrate with transition metal AQC consisting of 5 zero-valent silver metal atoms;
- wherein the coating step of the process of the present invention comprises:
- a) providing a composition consisting of: transition metal AQC consisting of 5 zero-valent silver metal atoms and water; wherein said transition metal AQC is in a concentration of 80 mg/L and a vinyl polymeric substrate;
- 20 b) spraying said composition to the surface of the vinyl polymeric substrate; and
- 25 c) drying the vinyl polymeric substrate of step (b) at room temperature.

In the context of the present invention “drying” means removing an excess of solvent by any method known in the art.

- 30 In a particular embodiment, the vinyl polymeric substrate comprises a vinyl polymer; wherein said vinyl polymer of the vinyl polymeric substrate is selected from the group consisting of polyethylene, polypropylene, polyisoprene (PI), polybutadiene, polystyrene, polyvinyl chloride (PVC), polyvinyl acetate (PVAc), polyvinyl alcohol (PVA), polyacrylate, polymethacrylate, polyacrylonitrile, polyvinylidene chloride,

polyvinylpyrrolidone, derivatives and/or combinations thereof; preferably polyisoprene (PI) and polyisoprene (PI) derivatives; more preferably polyisoprene (PI).

In a more preferred embodiment, the vinyl polymeric substrate is a polyisoprene (PI)
5 film.

Transition metal AQC's suitable for the process of the present invention are transition metal AQC's described above in any of their embodiments. Non-limiting examples of transition metal AQC's suitable for the process of the present invention are transition
10 metal AQC's comprising less than 200 metal atoms, wherein the transition metal of the transition metal AQC's is selected from Au, Ag, Co, Cu, Pt, Fe, Pd, Ni or their bi-metal and multi-metal combinations; preferably the transition metal of the transition metal AQC's is selected from Au, Ag, Co, Cu, Pt, Fe, Ni or their bi-metal and multi-metal combinations; more preferably is selected from Au, Ag, Cu, Pd or their bi-metal
15 and multi-metal combinations; even more preferably is selected from Au, Ag, Cu and their combination thereof. In a particular embodiment, the metal of the transition metal AQC's of the present invention are Ag or Cu; preferably Ag; more preferably Ag₅.

Polymeric composite obtainable by the process

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In a third aspect, the present invention is directed to a polymeric composite obtainable by the process of the present invention in any of its particular embodiments.

Uses

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In a further aspect, the present invention is directed to the use of transition metal AQC's as defined above in any of its particular embodiments, as stabilizers in vinyl polymers against the degradation of said vinyl polymers by oxidations processes; preferably in vinyl polymers selected from polyethylene, polypropylene, polyisoprene (PI),
30 polybutadiene, polystyrene, polyvinyl chloride (PVC), polyvinyl acetate (PVAc), polyvinyl alcohol (PVA), polyacrylate, polymethacrylate, polyacrylonitrile, polyvinylidene chloride, polyvinylpyrrolidone and derivatives; more preferably in polyisoprene (PI) polymers.

Transition metal AQC's of the present invention may be used as stabilizers alone or in combination with other stabilizer or mixtures of stabilizers known in the art. Transition metal AQC's of the present invention may be used as stabilizers in vinyl polymers by coating the surface of said vinyl polymers. In this way, the resulting vinyl polymer
5 comprises a coating or a coating layer comprising the transition metal AQC's of the present invention. In a particular embodiment, the transition metal AQC's of the invention are used as stabilizers alone.

In a preferred embodiment, transition metal AQC's of the present invention are used as
10 stabilizers in vinyl polymers, preferably as stabilizers in vinyl polymers against the degradation of said vinyl polymers by oxidation processes; more preferably as stabilizers in vinyl polymers against the degradation of said vinyl polymers by oxidation processes through a radical mechanism; even more preferably as stabilizers in vinyl polymers against the degradation of said vinyl polymers by oxidation processes
15 through a radical mechanism. In another particular embodiment, transition metal AQC's of the present invention are used as stabilizers in vinyl polymers particularly in processes such as those oxidation processes wherein vinyl polymers react with atmospheric oxygen through autoxidation process through mechanisms that depend on the vinyl polymer structure and external conditions like temperature and/or light
20 exposure. In a more preferred embodiment, transition metal AQC's of the present invention are used as stabilizers of polyisoprene (PI); preferably as stabilizers in films of polyisoprene (PI); more preferably as stabilizers of thin films of polyisoprene polymer.

25 In a preferred embodiment, the transition metal AQC's as defined above in any of its particular embodiments are used as stabilizers in vinyl polymers against light exposure; preferably against photoageing; more preferably against accelerated photoageing; even more preferably against constant irradiation applied with a xenon light at a power of 765 W m^{-2} with a cut-off at a wavelength below 295 nm.

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In a particular embodiment, the transition metal AQC's as defined above in any of its particular embodiments are used as stabilizers in vinyl polymers against the degradation of said vinyl polymers by oxidation processes caused by light exposure.

In the contest of the present invention, "light exposure" means outdoor daylight exposure as known in the art.

In a particular embodiment, the use of transition metal AQC's of the present invention as stabilizers in polymers reduces the degradation of said polymers caused by light exposure.

In the context of the present invention the term "stabilizer" in relation with vinyl polymers is understood as an additive commonly added to vinyl polymeric materials to inhibit or retard their degradation including radical degradation mechanisms such as those caused by oxidation. Non limiting examples of stabilizers known in the art that may be added in combination with the transition metal AQC's of the present invention are antioxidants such as radical scavengers, hydroperoxides scavengers, or antiozonants, light stabilizers such as UV absorbers, quenchers, or amine light stabilizers; acid scavengers; heat stabilizers; flame retardants; biocides and combinations thereof. Stabilizers may be incorporated in the vinyl polymer matrix or added to the surface of a substrate made of said vinyl polymer. A non-limiting example of a light stabilizer suitable to be used in combination with the transition metal AQC's of the present invention is a hindered amine light stabilizer (HALS) as known in the art; preferably a 2,2,6,6-tetramethyl-piperidine derivative.

In a particular embodiment, the transition metal AQC's as defined above in any of its particular embodiments are used as stabilizers in vinyl polymers; wherein said vinyl polymer is selected from the group consisting of polyethylene, polypropylene, polyisoprene (PI), polybutadiene, polyvinyl chloride (PVC), polyvinyl acetate (PVAc), polyvinyl alcohol (PVA), polyacrylate, polymethacrylate, polyacrylonitrile, polyvinylidene chloride, polyvinylpyrrolidone, derivatives and/or combinations thereof; particularly polyisoprene (PI).

Transition metal AQC's suitable for the uses of the present invention in any of its embodiments are those described above in any of the particular embodiments of the present invention.

EXAMPLES

The invention is illustrated by means of the following example that in no case limits the scope of the invention.

Example 1:

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The behavior of two samples under accelerated photoageing was studied in the present example. The samples were as follows:

- thin films of polyisoprene (PI) and
 - thin films of polyisoprene coated with 0.02 μg of Atomic Quantum Clusters (AQC₅) of 5 zero-oxidation-state silver atoms (Ag_5) per squared cm.
- 10

A water dispersion of 80 mg/L of Ag_5 AQC₅ was prepared. AQC₅ were applied to the surface of the thin substrates of polyisoprene (PI) by spraying a water dispersion of AQC₅ (80 mg/L) using an aerograph and spraying from a distance of 10 cm, perpendicularly to the surface. No changes in color of appearance of the PI substrates were observed after applying said AQC₅ to their surface.

15

The samples suffered standard accelerated photoageing for up to 55 hours carried out in a high-speed exposure unit Suntest CPS+ (Heraeus), equipped with a xenon light source consisting of a constant irradiation at a power of 765 W m⁻². A glass filter with cut-off at a wavelength below 295 nm was used to exclude radiation more energetic than that of outdoor daylight exposure. The maximum temperature reached by the samples during irradiation was 45 °C black panel temperature.

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The extent of oxidation was estimated from the ATR-FTIR spectra of the samples which were measured in a (ATR Smart Orbit TM with diamond crystal mounted on a Thermo Nicolet Nexus 5700 spectrometer) every 15 minutes. Figure 1a shows ATR-FTIR spectra of a pristine polyisoprene (PI) film (a') and of a polyisoprene (PI) film coated with 0.02 μg of Ag_5 AQC₅ per squared cm (b') after 50 h of accelerated photoageing. In figure 1a absorption bands ascribed to carbonyl (C=O) and hydroxyl (-OH) groups are shown.

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Figure 1b shows the intensity over photoageing time (h) of the carbonyl ATR-FTIR band at around 1720 cm⁻¹ normalized against the intensity of the absorption band at around 1445 cm⁻¹ ascribed to C-H deformation vibration band, which is constant during the early stages of the photoageing, for a pristine PI film (a') and for a PI film coated with Ag_5 (b').

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The normalized intensity of the band ascribed to carbonyl C=O groups was used for quantifying the relative extent and rate of oxidation of the samples. Results show that pristine (a') and treated (b') PI reached a constant level of oxidation after around 30 h of ageing (Figure 1b), indicating the occurrence of the same oxygen diffusion controlled process in both samples but with a lower oxygen incorporation in cluster-treated PI films (b'). Therefore, Figure 1b shows a slower formation of carbonyl groups in surface cluster treated PI (b') with respect to pristine PI. Additionally, Figure 1a and 1b shows that surface cluster treated PI was around 35 % less oxidized than pristine PI sample after 50 h of accelerated photoageing. Therefore, results showed that transition metal Atomic Quantum Clusters (AQC)s stabilize vinyl polymers, particularly in oxidation processes degradation. In addition, the sample of PI treated with clusters showed a constant level of oxidation (carbonyl groups intensity) between 30 h and 50 h of ageing (Figure 1b, (b')) indicating that no migration of AQC)s from the surface to the bulk of the polymer is produced during that period.

15

CLAIMS

1. A polymeric composite comprising:
 - a vinyl polymeric substrate; and
 - 5 – transition metal AQC comprising less than 200 zero-oxidation-state transition metal atoms;wherein said transition metal AQC are coating said vinyl polymeric substrate; wherein the transition metal AQC are coating said vinyl polymeric substrate in a concentration of less than 0.10 µg per square centimeter;
10 wherein the metal of the transition metal AQC is selected from Au, Ag, Co, Cu, Pt, Fe, Ni or their bi-metal an multi-metal combinations; and wherein transition metal AQC have a mean size of less than 2 nm.

2. The polymeric composite according to claim 1, wherein the vinyl polymeric
15 substrate comprises a vinyl polymer; wherein said vinyl polymer of the vinyl polymeric substrate is selected from the group consisting of polyethylene, polypropylene, polyisoprene (PI), polybutadiene, polystyrene, polyvinyl chloride (PVC), polyvinyl acetate (PVAc), polyvinyl alcohol (PVA), polyacrylate, polymethacrylate, polyacrylonitrile, polyvinylidene chloride,
20 polyvinylpyrrolidone, derivatives and/or combinations thereof.

3. The polymeric composite according to claim 2; wherein the vinyl polymeric substrate is polyisoprene (PI) and its derivatives.

- 25 4. The polymeric composite according to any of claims 1 to 3; wherein the vinyl polymeric substrate is a film.

5. The polymeric composite according to any of claims 1 to 4, wherein the transition metal AQC consist of less than 200 zero-oxidation-state transition
30 metal atoms.

6. The polymeric composite according to claim 5, wherein the transition metal AQC consist of less than 34 zero-oxidation-state transition metal atoms.

- 35 7. The polymeric composite according to any of claims 1 to 6, wherein the transition metal AQC are monodisperse.

8. The polymeric composite according to any of claims 1 to 7, wherein the metal of the transition metal AQC is selected from Au, Ag, Cu, or their bi-metal and multi-metal combinations.
- 5
9. The polymeric composite according to claim 8, wherein the metal of the transition metal AQC is Ag.
10. The polymeric composite according claim 6, wherein the transition metal AQC consist of less than 34 zero-oxidation-state transition metal atoms and wherein the metal of the transition metal AQC is Ag.
- 10
11. The polymeric composite according to claim 10, wherein the transition metal AQC consist of 5 zero-oxidation-state silver atoms Ag₅.
- 15
12. A process for preparing a polymeric composite comprising the following step:
– coating a vinyl polymeric substrate with a composition comprising transition metal AQC comprising less than 200 zero-oxidation-state transition metal atoms;
wherein the transition metal AQC are coating said vinyl polymeric substrate in a concentration of less than 0.10 µg per square centimeter;
wherein the metal of the transition metal AQC is selected from Au, Ag, Co, Cu, Pt, Fe, Ni or their bi-metal and multi-metal combinations; and
wherein transition metal AQC have a mean size of less than 2 nm.
- 20
- 25
13. The process according to claim 12, wherein the coating step is performed by dip coating, spray coating, vapor deposition or brush coating techniques.
- 30
14. The process according to claim 13, wherein the coating step is performed by spray coating techniques.
15. The process according to any of claims 12 to 14, wherein the transition metal AQC are in the composition in a concentration of below 100 mg/L.
- 35
16. The process according to any of claims 12 to 15, wherein the metal of the transition metal AQC is selected from Au, Ag, Cu, or their bi-metal and multi-

metal combinations.

17. The process according to claim 16, wherein the metal of the transition metal AQC is Ag.
- 5
18. The process according to any of claims 12 to 17, wherein the vinyl polymeric substrate comprises a vinyl polymer; wherein said vinyl polymer of the vinyl polymeric substrate is selected from the group consisting of polyethylene, polypropylene, polyisoprene (PI), polybutadiene, polystyrene, polyvinyl chloride (PVC), polyvinyl acetate (PVAc), polyvinyl alcohol (PVA), polyacrylate, 10 polymethacrylate, polyacrylonitrile, polyvinylidene chloride, polyvinylpyrrolidone, derivatives and/or combinations thereof.
19. The process according to any of claims 12 to 18, wherein the vinyl polymeric substrate is polyisoprene (PI) and polyisoprene (PI) derivatives.
- 15
20. A polymeric composite obtainable by the process as defined in any of claims 12 to 19.
- 20
21. Use of transition metal AQC as stabilizers in vinyl polymers against the degradation of said vinyl polymers by oxidation processes.
22. Use of transition metal AQC according to claim 21 against light exposure.
- 25
23. Use of transition metal AQC according to any of claims 21 or 22 wherein the transition metal AQC are coating the surface of said vinyl polymer.
24. Use of transition metal AQC according to any of claims 21 to 23, wherein said vinyl polymer is selected from the group consisting of polyethylene, 30 polypropylene, polyisoprene (PI), polybutadiene, polyvinyl chloride (PVC), polyvinyl acetate (PVAc), polyvinyl alcohol (PVA), polyacrylate, polymethacrylate, polyacrylonitrile, polyvinylidene chloride, polyvinylpyrrolidone, derivatives and/or combinations thereof.

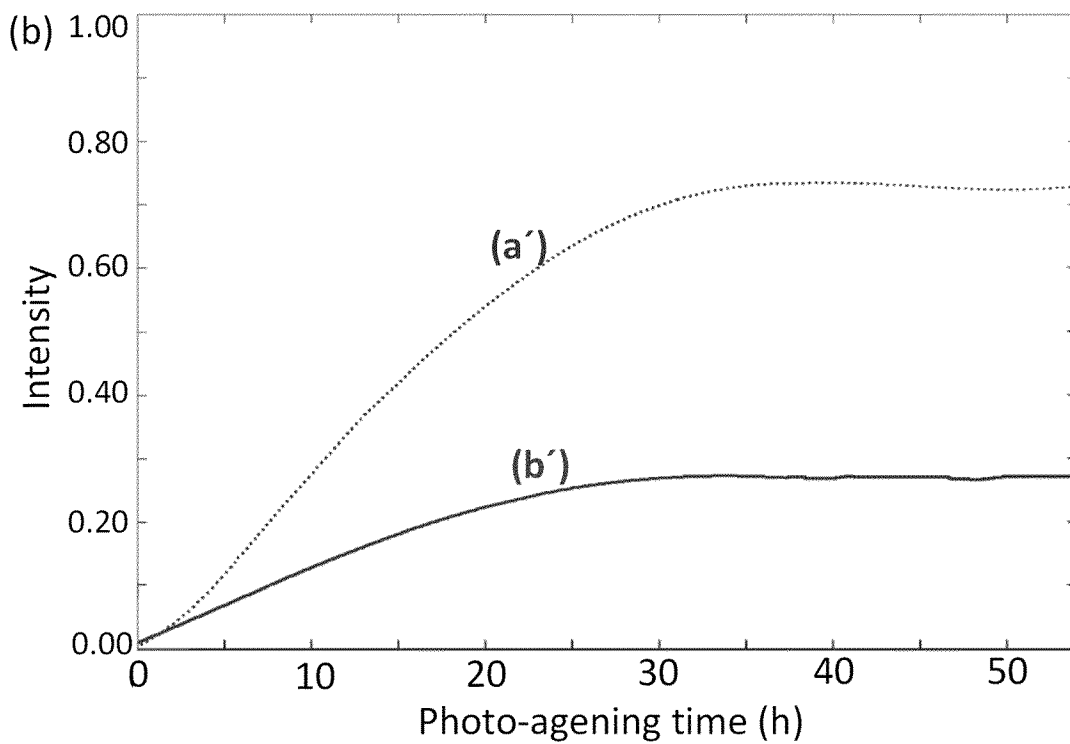
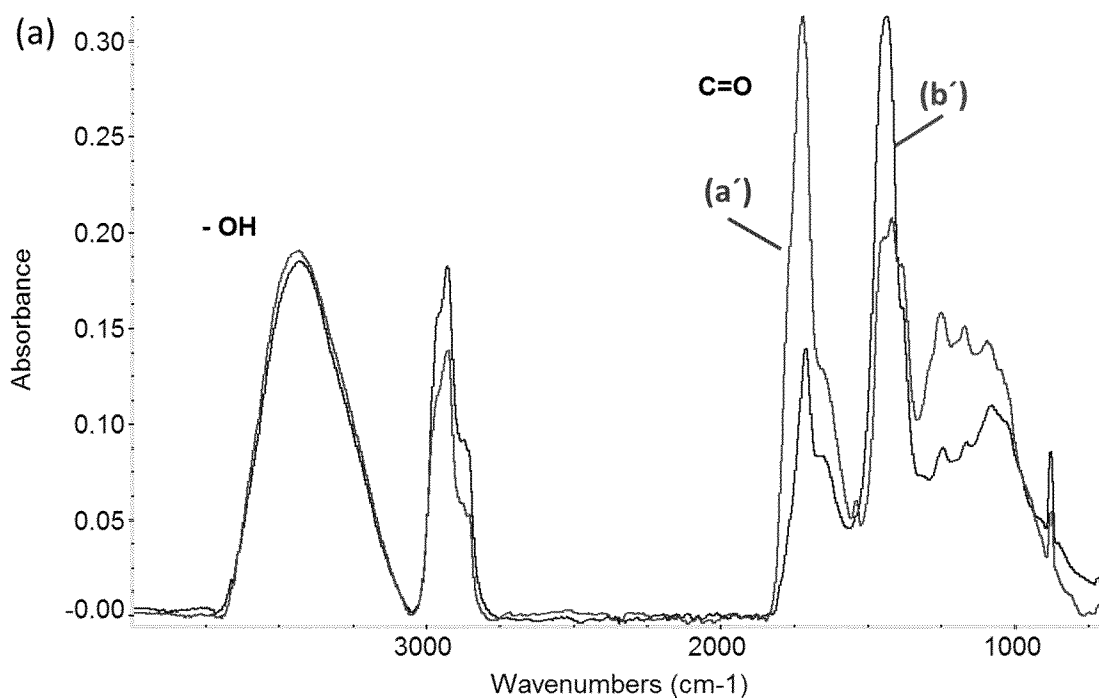


Figure 1

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2019/080364

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08K3/08 C08J7/06
ADD.
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)
C09J C08L C08K C08J

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, CHEM ABS Data

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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

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"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

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"&" document member of the same patent family

Date of the actual completion of the international search 5 December 2019	Date of mailing of the international search report 13/12/2019
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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 Gerber, Myriam
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INTERNATIONAL SEARCH REPORT

International application No
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