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(54) Title: PROCESS FOR PREPARING A MATERIAL WITH IMPROVED BARRIER PROPERTIES

(57) Abstract: The invention relates to a process for the preparation of a polymer-clay nano-composite composition comprising at least the following steps: • optionally preparing a first clay mixture by mixing at least one clay with a clay suitable medium, • preparing a polymerization mixture of one or more monomers in a suitable polymerization medium, • combining the first clay mixture and/or at least one solid clay with the polymerization mixture and mixing them so as to obtain a polymerization-clay mixture, • polymerizing the one or more monomers in the polymerization-clay mixture until the desired characteristics for the polymer are reached after which the polymerization is stopped, so as to obtain a polymer, • optionally preparing a second clay mixture by mixing at least one clay with a clay suitable medium, • adding the second clay mixture and/or at least one solid clay to the polymer obtained in a previous step and mixing them so as to obtain a polymer-clay nano-composite composition A, • optionally separating the polymer-clay nano-composite from the rest of the polymer-clay nano-composite composition A. The invention also relates to the obtained polymer-clay nano-composite, its use and a substrate coated with the polymer-clay nano-composite.



PROCESS FOR PREPARING A MATERIAL WITH IMPROVED BARRIER
PROPERTIES

5 The invention relates to a process for the preparation of a material with improved barrier properties. The invention further relates to the material with improved barrier properties and its uses.

 Materials with barrier properties are nowadays often used in the packaging industry so as to protect the materials and articles (together "contents") inside the packaging against unwanted influences coming from the outside. Generally
10 the packaging material needs to protect the contents inside against liquids, vapors and/or gases in the atmosphere on the outside of the package. Depending on the sensitivity of the contents the requirements put on the barrier properties of the packaging material are different. Some types of contents are sufficiently protected by a packaging material with low or medium barrier properties, while others need high barrier properties to keep
15 an acceptable quality over a sufficient period of time. Examples of classes of contents that are rather sensitive are electronic and medical materials and articles, further also a number of food and drinks are very sensitive. Examples in this last category are fruit-juice, beer, carbonated soft-drinks and food-stuff that needs to stay crispy for example chips and cereals.

20 To obtain materials with improved barrier properties sometimes concepts are applied that contain a metal or metal-oxide layer or a PVDC (polyvinylidene chloride) layer. However the metal layers that are used are non-transparent, cause environmental concern as they cause difficulties in recycling and the contents are not micro-waveable. Metal oxide layers are easily damaged,
25 expensive and are difficult to produce reliably. PVDC type of barrier films cause environmental concerns because of its chlorine content. Therefore there is a need for other and/or better materials with barrier properties. Even if the prior art materials will still be used in a packaging concept, it is worthwhile to reduce their content. Therefore there is a need to replace or at least decrease the share of these prior art materials.

30 Another way to improve barrier properties is described in WO 2007/106671 which is concerned with a polymeric material wherein organoclay is mixed with HDPE at levels under 4 weight percent. The mixing is performed on an extruder that is heated to a temperature sufficient to melt the HDPE. The organoclay is added to the molten HDPE either as a masterbatch in a thermoplastic polymer or as

such. However such a method of processing is not possible with all types of polymeric materials such as for example waterborne polymers.

A process for the incorporation of clay in an emulsion polymer is described in US 6.838.507. In US '507 an aqueous polymer clay nanocomposite
5 dispersion is prepared by combining a first aqueous reaction mixture comprising at least one ethylenically unsaturated monomer with a second aqueous reaction mixture comprising an at least partially exfoliated aqueous clay dispersion having at least one unmodified clay and at least one ethylenically unsaturated monomer and then
10 polymerizing the monomers in the presence of the clay.

It is known in the field of packaging that the addition of clay to
polymeric materials can improve the barrier properties of those polymeric materials. Generally, the higher the amount of clay incorporated into the polymeric material is, the larger the improvement in barrier properties is. However, by the addition of clay to a polymeric composition the viscosity of the composition will quickly increase. Mixing
15 equipment that is necessary in the production process will generally not be able to mix compositions above a certain viscosity. Therefore, from a practical point of view, the amount of clay that can be incorporated into the polymeric material is limited, thus limiting the improvement in barrier properties that can be obtained. However higher demands in the packaging industry make it necessary to make materials available with
20 again better barrier properties than the prior art. Here and hereinafter "material with improved barrier properties" and "substrate with improved barrier properties" are interchangeably used.

Therefore it is an object of the invention to provide a process for the preparation of a polymer-clay nano-composite composition which makes it possible to
25 use higher amounts of clay than the prior art processes. Such a process has now been found and comprises at least the following steps:

- optionally preparing a first clay mixture by mixing at least one clay with a clay suitable medium,
- preparing a polymerization mixture of one or more monomers in a suitable
30 polymerization medium,
- combining the first clay mixture and/or at least one solid clay with the polymerization mixture and mixing them so as to obtain a polymerization- clay mixture,

- polymerizing the one or more monomers in the polymerization- clay mixture until the desired characteristics for the polymer are reached after which the polymerization is stopped, so as to obtain a polymer,
- 5 • optionally preparing a second clay mixture by mixing at least one clay with a clay suitable medium,
- adding the second clay mixture and/or at least one solid clay to the polymer obtained in a previous step and mixing them so as to obtain a polymer-clay nano-composite composition A,
- 10 • optionally separating the polymer-clay nano-composite from the rest of the polymer-clay nano-composite composition A.

In case the steps that are herein referred to as “optional” are left out, the process would comprise at least the following steps:

- preparing a polymerization mixture of one or more monomers in a suitable polymerization medium,
- 15 • combining at least one solid clay with the polymerization mixture and mixing them so as to obtain a polymerization- clay mixture,
- polymerizing the one or more monomers in the polymerization- clay mixture until the desired characteristics for the polymer are reached after which the polymerization is stopped, so as to obtain a polymer,
- 20 • adding at least one solid clay to the polymer and mixing them so as to obtain a polymer-clay nano-composite composition A.

Additional advantages of this process, above the already mentioned higher loading of clay and the connected potential higher barrier properties, are that with the process according to the invention it is possible to add high amounts of clay without the polymerization mixture getting an unacceptably high viscosity or the mixture turning into a gel. A polymer that has an unacceptable high viscosity or has turned into a gel can't be further processed anymore and has therefore no use anymore, let alone as a packaging material. Another advantage of the process according to the invention is that the coatings that can be obtained from the polymer-clay nano-composite are optical transparent.

With “polymer-clay nano-composite composition” is meant a composition that at least comprises one polymer-clay nano-composite and at least one other component such as for example a suitable medium.

With "polymer-clay nano-composite" is meant a composite with polymer and clay particles wherein the clay has at least one of its dimensions, such as length, width or thickness, in the nanometer size range.

With "clay" is meant a clay mineral or phyllosilicate mineral. These types of materials are composed of layers of hydrated aluminum silicates. In between those layers, cations like sodium or potassium and water can be present. They include natural and synthetic clays. Natural clays include smectite clays, for example montmorillonite, saponite, hectorite, mica, vermiculite, bentonite, nontronite, beidellite, volkonskoite, magadite, kenyaite, kaolinite. Examples of synthetic clays include synthetic mica, synthetic saponite, synthetic hectorite.

With "clay suitable medium" is meant a medium that is able to disperse by itself or with the aid of a surfactant, the specific clay.

With "suitable polymerization medium" is meant a liquid medium that is either able to dissolve, disperse or emulsify the monomer and/or formed polymer so as to make the formation of a polymer from the monomers possible in an effective and efficient manner. The man skilled in the art of polymerizations knows and can easily determine a suitable polymerization medium for a given polymerization reaction.

With a solid clay is meant a clay that is in the solid state at room temperature and under normal atmospheric pressure.

The clay used in the preparation of the first clay mixture or the first solid clay can be the same as the clay used in the preparation of the second clay mixture or used as second solid clay. However this is not necessarily the case.

Examples of clays suitable for use in the present invention are natural and synthetic clays. Preferably synthetic clays are used. Clays used in the present invention can be a modified or an unmodified clay. Preferably the clay is an unmodified clay. It was surprisingly found that the desired barrier properties are better with an unmodified clay than with an organic- modified clay. Preferably Kunipia F, Cloisite Na⁺ or Nanocor PGW are used. Kunipia F is an unmodified clay that can be obtained from Kunimine Industries, Cloisite Na⁺ is an unmodified clay that can be obtained from Southern Clay Products, Nanocor PGW is an unmodified clay that can be obtained from Nanocor. More preferably Kunipia F is used in the present invention, because with Kunipia F the final film appearance and barrier properties are better.

Although, in principle, all kinds of clay are suitable for use in the present invention, it was found that clays with a certain particle size give better results in improving the barrier properties. Therefore a clay with a particle size of less than 10

μm is preferred. More preferred are clays with a particle size less than 8 μm , even more preferred with a particle size less than 6 μm . Most preferred are clays with a particle size of 0.1- 6 μm .

In case the particle size of the clay as obtained from a supplier is not
5 satisfactory in the sense that the amount of particles with relatively large dimensions is high, the clay can be "purified" so as to obtain a clay with an appropriate particle size and/or particle size distribution. A method to prepare a clay with appropriate particle size and/or particle size distribution is generally known to the man skilled in the art. Such a method is for example described in WO2007/101643.

10 The polymer-clay nano-composite can be characterized as being any of the following type, intercalated, exfoliated or combinations thereof. Intercalation means that the clay platelets are stacked with in between polymer. Intercalation can be either fully or partially. Exfoliation means that each platelet is individually dispersed. Exfoliation can be either fully or partially. For a high barrier property a high degree of
15 exfoliation of the clay is preferred.

The clay- suitable medium can comprise one or more liquids; in this manner the best combination of properties can be found so as to satisfy the process requirements. The medium can for example be water, an organic or inorganic solvent or a mixture of any of them. Thus it is possible to combine water with an organic
20 solvent so as to obtain desirable clay- dispersing power. Other combinations are of course also possible as the man skilled in the art will immediately understand and which he can determine without undue burden by simple routine experimentation. Non-limiting examples of other combinations are two or more organic solvents, two or more inorganic solvents, water and an inorganic solvent and an organic solvent combined
25 with an inorganic solvent. Preferably water or a combination of water with an organic solvent is used, most preferably water is used. Water is the preferred medium as it results in a good level of barrier properties in combination with a process that is favorable from an environmental and health point of view. Furthermore the combination of a hydrophilic medium such as for example water with an unmodified clay is
30 preferred.

In case the first and second clay are not the same the clay- suitable medium can be different for both clays. The clay –suitable medium is a medium that is able to disperse the clay. The mixing of the medium and the clay is performed until a homogeneous dispersion is obtained. This can generally take between 5 minutes and 2
35 hours. The man skilled in the art knows how to prepare such dispersion. To aid the

formation of the dispersion one or more surfactants can be added. However it is preferred to prepare the dispersion without the addition of surfactants.

The polymers used in the present invention can both be polymers that are formed in a polycondensation reaction between suitable monomers as well as
5 polymers that are formed by a polyaddition reaction.

Polymers formed in a polycondensation reaction are for example polyesters, polyamides, polyesteramides and polyethers. Polymers that are formed in a polyaddition reaction are for example vinyl polymers and vinyl oligomers. Hybrid
10 polymers can also be used, for instance urethane-acrylic hybrids, in which the urethane is formed by polyaddition and the acrylic polymer by a free-radical polymerization in the presence of the urethane. Blends of suitable polymers are also suitable.

By a "vinyl polymer" is generally meant a polymer derived from the addition polymerisation (normally by a free-radical process) of at least one olefinically unsaturated monomer. By a "vinyl monomer" is generally meant an olefinically
15 unsaturated monomer capable of undergoing free-radical polymerisation.

Examples of vinyl monomers include conjugated (optionally substituted) dienes; styrene and substituted styrenes; olefines such as ethylene or propylene; vinyl halides; vinyl esters such as vinyl acetate, vinyl propionate, vinyl laurate, and vinyl esters of versatic acid such as VeoVaTM 9 and VeoVaTM 10 (VeoVa is
20 a trademark of Shell); heterocyclic vinyl compounds, dialkyl esters of mono-olefinically unsaturated dicarboxylic acids (such as di-n-butyl maleate and di-n-butyl fumarate; vinyl ethers; and, in particular, esters of acrylic acid and methacrylic acid of formula:



where R¹ is H or methyl and R² is optionally substituted alkyl of 1 to 20 carbon atoms
25 (more preferably 1 to 8 carbon atoms) or cycloalkyl of 5 to 12 ring carbon atoms. Further specific examples of such monomers include alkyl esters and (chloro)alkyl esters such as methyl acrylate, ethyl acrylate, n-propyl acrylate, n-butyl acrylate, i-butyl acrylate, t-butyl acrylate, n-octyl acrylate, 2-ethylhexyl acrylate, lauryl acrylate, isopropyl acrylate, isobornyl acrylate, cyclohexyl acrylate, methyl α-chloroacrylate, n-propyl α-chloroacrylate, n-butyl α-chloroacrylate, β-chloroethyl acrylate, β-chlorobutyl
30 acrylate, methyl methacrylate, ethyl methacrylate, n-propyl methacrylate, isopropyl methacrylate, n-butyl methacrylate, i-butyl methacrylate, t-butyl methacrylate, isobornyl methacrylate, cyclohexyl methacrylate, 2-ethylhexyl methacrylate, octyl methacrylate, lauryl methacrylate, diethyl maleate, diethyl fumarate; vinyl esters such as allyl acetate,

allyl chloroacetate, methallyl acetate, vinyl acetate, isopropenyl acetate; vinyl halides such as vinyl chloride, vinylidene chloride, allyl chloride, 1,2-dichloropropene-2, methallyl chloride, trifluoroethyl(meth)acrylate and trichloroethylene; nitriles such as acrylonitrile and methacrylonitrile; vinyl aryls such as styrene, α -methyl styrene, o-methyl styrene, m-methyl styrene, p-methyl styrene, pentachlorostyrene, o-chlorostyrene, m-chlorostyrene, p-chlorostyrene and p-cyanostyrene; conjugated dienes or chlorodienes such as butadiene and chloroprene; and vinyl-substituted heterocyclic imines such as 2-vinyl-pyridine and vinyl carbazole. Other vinyl monomers include di-hydroxyalkyl (meth)acrylate adducts of organic diisocyanates, such as the di-hydroxyethyl methacrylate adduct of a C_9H_{18} diisocyanate sold by Rohm GmbH as PLEX 6661.0.

Other monomer(s) which may also be used to form vinyl polymers are those bearing a functional group(s) (and not already mentioned above). These can include for example hydroxyl functional monomers such as hydroxyethyl (meth)acrylate, hydroxylpropyl (meth)acrylate, hydroxylbutyl (meth)acrylate, and olefinically unsaturated amides such as acrylamide, and methacrylamide. Other groups include carbonyl functional groups which include, unless otherwise specified, the carbonyl group of an aldehyde group or ketone group (and includes an enolic carbonyl group such as is found for example in an acetoacetyl group). Preferred carbonyl group containing monomer(s) are selected from diacetone (meth)acrylamide (DA(M)AM), (meth)acrolein, vinyl alkyl ketones with 1 to 20 C atoms in the alkyl group, and acetoacetoxyl ethylmethacrylate. Also dialkylamino functional monomers can be used like dimethylamino ethylmethacrylate.

The amount of such functional monomer(s) incorporated generally lies between 0.1 to 20 wt%, preferably 0.1 to 10 wt%, more preferably 0.1 to 3 wt% based on total monomer composition. In most cases, however, no such functional monomer(s) is used.

The polymer for use in the invention may also contain difunctional monomers like allyl methacrylate, tetraethylene glycol methacrylate and divinyl benzene or tri- or tetra functional (meth)acrylate. These monomers are used between 0 to 2 wt% and more preferably 0 to 0.5 wt%.

The vinyl monomer(s) containing an acid functional group can be used as well. These preferably are olefinically unsaturated monocarboxylic or dicarboxylic acids, examples of which include acrylic acid, methacrylic acid, 2-carboxyethyl acrylate, fumaric acid, maleic acid, itaconic acid, and mono-substituted

C1-C20 alkyl esters of dicarboxylic acids. The amount of unsaturated carboxylic acids generally lies within the range 0-50 wt%, preferably 1-30 wt%, more preferably 2-20 wt% and most preferably 3-10 wt%. Preferred unsaturated carboxylic acids are methacrylic acid and acrylic acid.

5 Particularly preferred are vinyl polymers made from a monomer system comprising at least 60 wt% of one or more vinyl monomers of the formula $\text{CH}_2=\text{CR}_1\text{COOR}_2$ defined above, styrene, α -methyl styrene and acrylonitrile. Such preferred vinyl polymers are defined herein as acrylic polymers. More preferably, the vinyl monomer system contains at least 70 wt% of such monomers and particularly at
10 least 80 wt%. The other monomers in such acrylic polymers (if used) may include one or more of the other vinyl monomers mentioned above and/or may include ones different to such other monomers. More preferred monomers include methyl (meth)acrylate, ethyl (meth)acrylate, n-butyl (meth)acrylate, styrene and 2-ethylhexyl (meth)acrylate. Most preferred monomers include methyl (meth)acrylate, ethyl (meth)
15 acrylate as it appeared that those monomers in combination with the clay lead to better barrier properties.

In a particularly preferred embodiment the polymerization mixture comprises an aqueous dispersion of:

- (i) 2 to 20 wt%, of at least one unsaturated carboxylic acid
- 20 (ii) 40 to 80 wt% of a unsaturated vinyl monomers being ethyl (meth)acrylate, and/or methyl (meth)acrylate.
- (iii) 0 to 40 wt%, of monomers other than i) and ii)

where (i) + (ii) + (iii) add up to 100 wt%.

The vinyl polymers suitable for use in the invention are normally
25 made using free radical addition polymerisation in an aqueous emulsion polymerisation process to form an aqueous polymer emulsion. Such an aqueous emulsion polymerisation process is, in itself, well known in the art and need not be described in great detail. Suffice to say that such a process involves dispersing the vinyl monomers in an aqueous medium and conducting polymerisation using a free-radical yielding
30 initiator and (usually) appropriate heating (e.g. 30 to 120 °C) and agitation (stirring) being employed. The aqueous emulsion polymerisation can be effected using one or more conventional emulsifying agents, these being surfactants. Anionic and non-ionic surfactants and combinations of the two types are preferred. Chain transfer agents (e.g. mercaptanes or suitable cobalt chelate complexes) may be included if desired to
35 control molecular weight.

Suitable free-radical-yielding initiators include inorganic peroxides such as K, Na or ammonium persulphate, hydrogen peroxide, or percarbonates; organic peroxides, such as acyl peroxides including e.g. benzoyl peroxide, alkyl hydroperoxides such as t-butyl hydroperoxide and cumene hydroperoxide; dialkyl peroxides such as di-t-butyl peroxide; peroxy esters such as t-butyl perbenzoate and the like; mixtures may also be used. The peroxy compounds are in some cases advantageously used in combination with suitable reducing agents (redox systems) such as Na or K pyrosulphite or bisulphite and iso-ascorbic acid. Metal compounds such as Fe.EDTA (EDTA is ethylene diamine tetracetic acid) may also be usefully employed as part of the redox initiator system. Azo functional initiators may also be used. Preferred azo initiators include azobis-(isobutyronitrile) and 4,4'-azobis(4-cyanovaleric acid). The amount of initiator or initiator system used is conventional, e.g. within the range 0.05 to 4 wt% based on the total vinyl monomers used. Preferred initiators include ammonium persulphates, sodium persulphates, potassium persulphates, azobis(isobutyronitrile), 4,4'-azobis(4-cyanovaleric acid) and/or t-butyl hydroperoxide.

Suitable chain transfer agents include mercaptans such as n-dodecylmercaptan, n-octylmercaptan, t-dodecylmercaptan, mercaptoethanol, iso-octyl thioglycolate, C2 to C8 mercapto carboxylic acids and esters thereof such as 3-mercaptopropionic acid and 2-mercaptopropionic acid; and halogenated hydrocarbons such as carbon tetrabromide and bromo- trichloromethane. Preferably ≤ 5 wt%, more preferably ≤ 3 wt% and most preferably no chain transfer agent based on the weight of vinyl monomers required is used.

The aqueous vinyl polymers can be prepared by any free radical polymerisation method known in the art. Emulsion polymerisation is preferred. The polymers can be prepared using the various polymerisation methods known in the art such as single batch, sequential and gradient polymerisation, also commonly known as a power feed polymerisation. If desired, a preformed or in-situ formed seed can be used. In-line mixing for two or more of the materials employed may also be used.

The vinyl polymers for use in the process according to the invention can also be prepared using a surfactant-free emulsion polymerisation process. In this process, alkaline soluble low molecular weight polymers are used as surfactants in the presence of which a polymerisation is performed. This results in so-called oligomer-supported polymer systems. These alkaline soluble oligomers can be prepared by emulsion, solution or by bulk polymerization.

The suitable polymerization medium can comprise one or more than one liquid: in this manner the best combination of properties can be found so as to satisfy the process requirements. The medium can for example be water, an organic or inorganic solvent or a mixture of any of them. Thus it is possible to combine water with
5 an organic solvent so as to obtain desirable dispersing power. Other combinations are of course also possible as the man skilled in the art will immediately understand and which he can determine without undue burden by simple routine experimentation. Non-limiting examples of other combinations are two or more organic solvents, two or more inorganic solvents, water and an inorganic solvent and an organic solvent combined
10 with an inorganic solvent. Preferably water or a combination of water with an organic solvent is used, most preferably water is used.

If an organic solvent(s) is used in combination with water, less than 50 wt%, preferably less than 30 wt%, more preferably less than 10 wt%, even more preferably less than 5 wt% and most preferably less than 0.5 wt% solvent(s) is used.

15 It is preferred to choose the polymerization medium and the clay-suitable medium so as to have a combination of liquids that mix. Although it is not strictly necessary, it is advantageous to have such a combination as it will improve the stability of the reaction medium. A non-mixing combination of a suitable polymerization medium and a clay- suitable medium can lead to instability, which makes the
20 preparation process less predictable and therefore the products (or their properties) obtained from the process can vary.

The first clay mixture, when desired, is prepared by mixing at least one clay with a clay suitable medium. It is possible to use only one type of clay in this step, however it is also possible to use two or more types of clay. It is preferred to use
25 in this step only one type of clay, because in that case process economics are generally more favorable.

The clay can be mixed with the suitable medium under normal shear or under high shear conditions. When using a high shear process, preferably a homogenization process is used in which the clay mixture is prepared typically at a
30 shear rate of 10,000 - 20,000 rpm. When a normal shear mixing process is used the shear rate will generally lie in the range of 50-1000 rpm.

While making the mixture of the clay and the suitable medium, surfactants to aid the preparation can be used, however it is preferred to use no surfactants as their absence facilitates the further preparation process. Further it has
35 been found that the absence of a surfactant can be beneficial to the barrier properties

of the final coating. When necessary anionic, non-ionic and/or cationic surfactants can be used. A suitable choice is easily made by the man skilled in the art. Commercially available clay dispersants like Anti-Terra® 206 or Disperbyk®, both available from Byk Chemie can be used to prepare the clay mixture. However, the amount of clay
5 dispersant used should not influence the barrier properties.

A suitable range for the solid content of the clay mixture can be 0.1-40 wt%, preferably 1.0-30 wt%, more preferably 2.0-20 wt%, more preferably 2.0-10 wt% and most preferably 1.0-5 wt%.

The polymerization mixture is prepared by combining one or more
10 monomers with a suitable polymerization medium. The combining of the monomer(s) with the medium is not particularly relevant as long as both are mixed well. This can be reached by means known to the man skilled in the art.

To obtain a polymerization- clay mixture, the polymerization mixture is combined with the first clay mixture and/or at least one solid clay, followed by mixing. It
15 is possible to start with the clay mixture that was prepared in the first optional step or it is possible to start with at least one solid clay. Both possibilities will result in the formation of a polymerization- clay mixture. It is preferred however to start with the first clay mixture as in that case the mixing of the clay or clays and the monomer or monomers in the polymerization mixture is easier.

20 When the clay or clays are combined with the polymerization mixture they are mixed. Mixing can occur by techniques generally known in the art. Examples of suitable mixing techniques are blending or in-line mixing. During the mixing step the viscosity of the combination can increase.

The desired polymer is obtained by polymerization of the monomers
25 present in the polymerization mixture. It is not necessary to polymerize all monomers present. It is also possible to polymerize only a part of the monomers, thereby leaving the other part of the monomers unused. Preferably the polymerization is brought to its end by the consumption of all of the monomers as the presence of even small amounts of monomers can give rise to unwanted properties such as for example smell.
30 Additionally the presence of unreacted monomers is unwanted from the point of view of health, environment and safety. The polymerization is stopped when the characteristics for the desired polymer are reached.

Optionally a second clay mixture is prepared by mixing at least one
clay with a, for that clay, suitable clay medium. The second clay can be a clay of the
35 same type as the first used clay or it can be a different type of clay. Either this second

clay mixture and/or the at least one solid clay are added to the polymer obtained in a previous step, followed by mixing upon which a polymer-clay nano-composite composition A is formed. This polymer-clay nano-composite composition A will generally at least comprise the polymer-clay nano-composite and at least one of the media used in this and/or the previous steps. The mixing of the second clay and the polymer are effected through generally available apparatus and techniques, well-known to the man skilled in the art.

When desired the polymer-clay nano-composite can be separated from the rest of the polymer-clay nano-composite composition A. This separation step is advantageous when the polymer-clay nano-composite will be used or stored as a solid. However when the polymer-clay nano-composite will be used or stored as such it is not necessary to separate it.

In the process according to the invention it is thus essential that the total amount of clay is added in at least two stages as is also described above. The ratio of clay that is incorporated in the first mixture (first stage) to the clay that is incorporated in the second (and further if any) mixture (second stage) can be chosen between wide ranges. A suitable range for the ratio is 10:1 to 1:10. Preferably a range of 8:1 to 1:8, more preferably 5:1 to 1:5, most preferably 3:1 to 1:3 is chosen.

The total amount of clay incorporated in the polymer-clay nano-composite can be chosen so as to fulfill the requirements that are put on the barrier properties. Depending on the combination of clay and polymer up to approximately 50 wt% of clay can be reached. Generally the amount is between 1-40 wt%. Preferably the amount incorporated is between 1.5 and 30 wt%, more preferably between 2 and 25 wt% and most preferred between 3 and 20 wt%. The amount referred to here is the amount of solid clay compared to the total amount of solid polymer-clay nano-composite.

In another embodiment of the invention the process as described above is modified in that at least a second addition of monomer is envisaged at the stage when the second clay mixture is prepared. In this manner the final polymer can be tailored to specific needs in that the polymer formed in the first polymerization stage is based on a different monomer or different mixture of monomers than the polymer formed in the second or further polymerization stage(s). With "different mixture of monomers" both the situation that different monomers are present in the second mixture compared to the monomers in the first mixture is meant as well as the situation where the same monomers are used but in a different ratio. In this embodiment the

process for the preparation of a polymer-clay nano-composite composition comprises at least the following steps:

- A. optionally preparing a first clay mixture by mixing at least one clay with a clay suitable medium,
- 5 B. preparing a first polymerization mixture of one or more monomers in a suitable polymerization medium,
- C. combining the first clay mixture and/or at least one solid clay with the first polymerization mixture and mixing them so as to obtain a first polymerization- clay mixture,
- 10 D. polymerizing the one or more monomers in the first polymerization- clay mixture until the desired characteristics for the first stage polymer are reached, after which the polymerization is stopped so as to obtain a first stage polymer,
- E. optionally preparing a further clay mixture by mixing at least one clay with a clay suitable medium,
- 15 F. preparing a further polymerization mixture of one or more monomers in a suitable further polymerization medium,
- G. adding the further polymerization mixture and the optional further clay mixture and/or at least further solid clay to the first stage polymer and mixing them so as to obtain a further polymer- clay mixture,
- 20 H. polymerizing the one or more monomers in the further polymerization- clay mixture until the desired characteristics for the polymer are reached, after which the polymerization is stopped so as to obtain a polymer-clay nano-composite composition B,
- 25 I. optionally separating the polymer-clay nano-composite from the rest of the polymer-clay nano-composite composition B,
- J. optionally repeating the steps E-J.

Preferably the process for the preparation of a polymer-clay nano-composite composition makes use of only one additional clay mixture or solid clay. In
30 such a situation the process for the preparation of a polymer-clay nano-composite composition comprises at least the following steps:

- optionally preparing a first clay mixture by mixing at least one clay with a clay suitable medium,

- preparing a first polymerization mixture of one or more monomers in a suitable polymerization medium,
- combining the first clay mixture and/or at least one solid clay with the first polymerization mixture and mixing them so as to obtain a first polymerization-
5 clay mixture,
- polymerizing the one or more monomers in the first polymerization- clay mixture until the desired characteristics for the first stage polymer are reached, after which the polymerization is stopped so as to obtain a first stage polymer,
- optionally preparing a second clay mixture by mixing at least one clay with a
10 clay suitable medium,
- preparing a second polymerization mixture of one or more monomers in a suitable second polymerization medium,
- adding the second polymerization mixture and the optional second clay mixture and/or at least a second solid clay to the first stage polymer and
15 mixing them so as to obtain a second polymer- clay mixture,
- polymerizing the monomers in the second polymerization- clay mixture until the desired characteristics for the polymer are reached, after which the polymerization is stopped so as to obtain a polymer-clay nano-composite composition B,
- optionally separating the polymer-clay nano-composite from the rest of the
20 polymer-clay nano-composite composition B.

In case the steps that are herein referred to as “optional” are left out, the process comprises at least the following steps:

- preparing a first polymerization mixture of one or more monomers in a suitable
25 polymerization medium,
- combining the at least one solid clay with the first polymerization mixture and mixing them so as to obtain a first polymerization- clay mixture,
- polymerizing the one or more monomers in the first polymerization- clay mixture until the desired characteristics for the first stage polymer are reached, after which the polymerization is stopped so as to obtain a first stage polymer,
30
- preparing a second polymerization mixture of one or more monomers in a suitable second polymerization medium,

- adding the second polymerization mixture and the at least second solid clay to the first stage polymer and mixing them so as to obtain a second polymer-clay mixture,
- polymerizing the monomers in the second polymerization- clay mixture until the desired characteristics for the polymer are reached, after which the polymerization is stopped so as to obtain a polymer-clay nano-composite composition B.

For description of individual elements and preferences, reference is made to what is described in connection with the other Embodiments of the invention.

The present invention also relates to a polymer-clay nano-composite or polymer-clay nano-composite composition obtainable by the process according to the invention. The maximum loading of clay in this polymer-clay nano-composite or polymer-clay nano-composite composition is higher than in prior art materials.

The polymer-clay nano-composite or polymer-clay nano-composite composition according to the invention is for example very suitable for use as coating on a substrate. Therefore the invention also relates to the use of the polymer-clay nano-composite or polymer-clay nano-composite composition according to the invention to coat a substrate. By applying it to a substrate certain properties of the substrate can be improved. Examples of the properties that can be improved by the use of the polymer-clay nano-composite or polymer-clay nano-composite composition according to the invention are amongst others barrier properties and flame retardancy. Especially advantageous is the enhancement of the barrier properties.

The invention also relates to a substrate coated with a polymer-clay nano-composite or polymer-clay nano-composite composition according to the invention. These substrates with enhanced barrier properties are very suitable for use in food packaging and packaging of other perishables, packaging of medical instruments, packaging of medicaments and packaging of electronic instruments or electronic parts.

Suitable substrates for use in combination with the polymer-clay nano-composite or polymer-clay nano-composite composition according to the invention are not particularly critical and the choice will mainly be determined by the field of application and the processing techniques used in that field. Examples of suitable substrates are paper or paperboard, consolidated wood products, glass, plastic, wood, metal, primed or painted surfaces, ceramics, leather. To take advantage

of the improvement of the barrier properties by the application of the polymer-clay nano-composite or polymer-clay nano-composite composition especially preferred substrates are glass and plastic. These substrates can be used as such or the substrate can be pre-treated, for example a primer can be applied or a printing layer etc. The man skilled in the art knows how to pre-treat a substrate and how to determine the best method of pre-treatment. Examples of plastic materials are polyolefin, polyester, polyether, polyamide, polystyrene and polycarbonate. In food packaging often polyolefins and polyesters are used. Examples of polyolefins are polyethylene and polypropylene. Examples of polyesters are polyethelene terephthalate and polybutylene terephthalate. The substrate can be in various forms and is not particularly relevant and will generally be determined by the final use envisaged. Examples are film, sheet and plastic composites.

The invention therefore also relates to a process to improve the barrier properties of a substrate comprising at least the following step:

- applying the polymer-clay nano-composite composition B or the polymer-clay nano-composite composition A obtained by the process according to the invention onto the substrate.

This process can comprise the optional step of pre-treating the surface and/or the optional step of removing the polymer-clay nano-composite medium. In this process for improving the barrier properties of a substrate, either the polymer-clay nano-composite composition as obtained in the process according to the invention can be used or, when in that process the polymer-clay nano-composite is separated from the medium, the polymer-clay nano-composite can be mixed with a suitable polymer-clay nano-composite medium that not necessarily needs to be the same as the medium used in the initial process. This is of course an optional step. When the optional steps described here are considered, the process to improve the barrier properties of a substrate comprises at least the following steps:

- optionally pre-treating the substrate,
- optionally mixing the polymer-clay nano-composite obtained by the process according to the invention with a suitable polymer-clay nano-composite medium so as to obtain a polymer-clay nano-composite composition B,
- applying the polymer-clay nano-composite composition B or the polymer-clay nano-composite composition A obtained by the process according to the invention onto the substrate,

- optionally removing the polymer-clay nano-composite medium.

The man skilled in the art knows or can easily determine how the polymer-clay nano-composite composition A or B is best applied onto the substrate. Examples of application methods are, without being limited to them, brushing, spraying, roll-coating, doctor-blade application, printing methods, curtain coating or extrusion. Of course also combinations can be used.

The invention also related to the substrate with improved barrier properties obtainable by this process.

The use of the polymer-clay nano-composite or polymer-clay nano-composite composition according to the invention improves especially the barrier properties of a substrate on which it is applied against oxygen, carbon dioxide, water and/ or water vapor. A substrate coated with a polymer-clay nano-composite according to the invention has an oxygen barrier that is a factor 2-10 better than the uncoated substrate. This improvement factor can easily be reached in the two-step process. Already after the first step an improvement in barrier properties can be reached: a factor 1.5-3 can easily be reached. With first and second step is here referred to the addition of clay in the first and second mixture.

The present invention also relates to the use of the polymer-clay nano-composite or polymer-clay nano-composite composition according to the invention. The polymer-clay nano-composite or polymer-clay nano-composite composition according to the invention can advantageously be used in blends with for example polymers. They can also be used in coating all kind of surfaces.

The present invention is illustrated with the following non-limiting examples. In all examples, the wt% clay given refers to the amount of solid clay on solid polymer and clay.

Preparation of the clay mixture

A 4 wt% solid Kunipia F clay dispersion was prepared by adding, under ambient conditions, batchwise 4 gram Kunipia F to 100 ml demineralised water using a Heidolph RZR 2050 stirrer with a stirring speed of 300-500 rpm. When the first amounts of Kunipia F were added the stirring speed was set at 300 rpm. When the amount of Kunipia F increased the stirring speed was increased to 500 rpm.

Preparation of the polymer-clay nano-composite compositionExample 1Polymer 1

A 2L three-neck round bottom glass reactor, equipped with a stirrer,
5 N₂ inlet, thermometer and baffles was loaded with 215.0 gram demineralised water,
76.9 gram of Indurez SR10PG (an alkaline soluble low molecular weight polymer
available from Indulor GmbH) and 12.7 gram ammonia (25 wt%). The reactor and its
contents were kept at 80 °C until a clear solution was obtained. Next 140.8 gram
demineralised water and 494.4 gram of the 4 wt% dispersion of Kunipia F were added.

10 In a dropping funnel an emulsified monomer feed was prepared by
stirring 56.6 gram water, 2.8 gram sodium lauryl sulphate, 91.6 gram ethyl acrylate
(EA), 78.0 gram methyl methacrylate (MMA) and 0.9 gram dodecyl mercaptane (the
monomer feed is kept at ambient temperature).

An initiator feed was prepared by dissolving 0.9 gram ammonium
15 persulphate and 0.4 gram ammonia (25%) in 28.3 gram demineralised water.

An initiator shot was prepared by dissolving 2.6 gram ammonium
persulphate and 0.8 gram ammonia (25%) in 3.1 gram water. The temperature was
raised to 85 °C and the initiator shot was added to the reactor.

After 10 minutes the monomer and initiator feeds were added over a
20 period of 120 minutes. Afterwards, 5.8 gram demineralised water was added.

Next, the mixture was cooled to room temperature and 2.4 gram
Proxel Ultra 10 (1,2-benzisothiazolin-3-one available from Arch Chemicals) was added.
Finally the reaction mixture was collected. The obtained polymer dispersion in this step
had a solid content of 19.2 wt%, the pH was 7.3, the Brookfield viscosity was 160
25 m.Pa.s. and the amount of coagulum was < 0.10 wt%. The amount of Kunipia F on
polymer and clay was 8.3 wt%.

Step 2: Post-addition of nanoclay

To 300 gram of the Polymer 1 dispersion obtained in step 1, a 4 wt%
30 Kunipia F dispersion was added under normal stirring until finally 23.2 wt% Kunipia F
was added (based on polymer and clay). Thus in this particular example 14.9 wt%
Kunipia F was post- added in step 2. The final polymer dispersion as obtained in
Example 1, had a solid content of 11.2 wt%, the pH was 7.5, the Brookfield viscosity
was 1092 m.Pa.s. and the amount of coagulum was <0.10 wt%.

Viscosity determination

All viscosities were determined by a Brookfield LVDV-I viscometer using spindle II at a rotation speed of 60 rpm at 20 °C.

5 Example 2 and 3

Examples 2 and 3 were prepared according to the same two-step procedure used for Example 1. The amount of nanoclay used in each example is given in Table 1.

Table 1

	Kunipia added by step 1 (wt%)	Kunipia added by step 2 (wt%)	Total amount of Kunipia added (wt%)	Solids content dispersion (%)	Viscosity (m.Pa.s.)	pH
Polymer 1	8.3	0	8.3	19.2	160	7.33
Example 1	8.3	14.9	23.2	11.2	1092	7.45
Polymer 2	2.0	0	2.0	20.0	47	7.27
Example 2	2.0	8.4	10.4	15.4	604	7.27
Polymer 3	5.0	0	5.0	20.0	366	7.29
Example 3	5.0	5.7	10.7	16.7	974	7.91

10 Example 4Polymer 4

A 2L three-neck round bottom glass reactor, equipped with a stirrer, N₂ inlet, thermometer and baffles was loaded with 388.2 gram demineralised water, 1.6 gram of a nonylphenol ethoxylated phosphate surfactant, 0.6 gram NaHCO₃, 0.2 gram ammonium persulphate and 150.0 gram of a 4 wt% dispersion of Kunipia F.

In a dropping funnel an emulsified monomer feed was prepared by stirring 110.3 gram water, 5.8 gram of a nonylphenol ethoxylated phosphate surfactant, 0.3 gram NaHCO₃, 12.1 gram methacrylic acid (MAA), 86.3 gram ethyl acrylate (EA), 195.6 gram methyl methacrylate (MMA) and 3.2 gram dodecyl mercaptan (the monomer feed is kept at ambient temperature).

An initiator feed was prepared by dissolving 0.7 gram ammonium persulphate in 55.2 gram demineralised water. The temperature was raised to 85 °C.

At 70°C, 10 wt% of the monomer feed was pre-charged and the reaction mixture was heated to 85 °C.

At 85 °C the monomer feed was added over a period of 60 minutes and the initiator feed was added over a period of 70 minutes. 12.1 gram demineralised water was added. The reaction mixture was kept at 85 °C for 30 minutes.

Next a solution of 55.2 gram ammonia (25%) in 138.0 gram demineralised water was added slowly and the reaction mixture was stirred for 165 minutes at 85 °C followed by cooling to 40 °C. Next, 3.0 gram Proxel Ultra 10 was added and the mixture was cooled to room temperature.

Finally the reaction mixture was filtered and collected. The final polymer dispersion had a solid content of 20.0 wt%, the pH was 10.2, the Brookfield viscosity was 168 m.Pa.s. and the amount of coagulum was < 0.10 wt%. The amount of Kunipia F on solid polymer was 2.0 wt%.

15 Step 2: Post-addition of nanoclay

To 300 gram of the Polymer 4 dispersion obtained in step 1 of Example 4, a 4 wt% Kunipia F dispersion was added under normal stirring until finally 10.4 wt% Kunipia F was added on polymer and clay. In this particular example 8.4 wt% Kunipia F was post- added on solids. The final polymer dispersion Example 4, had a solid content of 15.4 wt%, the pH was 10.09, the Brookfield viscosity was 489 m.Pa.s. and the amount of coagulum was <0.10 wt%.

Example 5 and 6

Exampes 5 and 6 were prepared according to the same two-step procedure used for Example 4. The amount of nanoclay used in each Example is given in Table 2.

Table 2

	Kunipia added by step 1 (wt%)	Kunipia added by step 2 (wt%)	Total amount of Kunipia added (wt%)	Solids content dispersion (%)	Viscosity (m.Pa.s.)	pH
Polymer 4	2.0	0	2.0	20.0	168	10.18
Example 4	2.0	8.4	10.4	15.4	489	10.09
Polymer 5	2.7	0	2.7	20.0	278	10.22
Example 5	2.7	7.4	10.1	17.6	432	10.16
Polymer 6	13.6	0	13.6	11.6	257	9.95
Example 6	13.6	8.3	21.9	6.8	206	9.73

Examples 7 and 8: use of pigment dispersants

- A 4 wt% Kunipia F dispersion was prepared according to the procedure described above. To the Kunipia F dispersion, 4 wt% of Disperbyk or 4 wt% of Anti-Terra were added (both are commercially available from Byk Chemie, Germany). The resultant dispersion was used in Example 7 and 8.

- For Examples 7 and 8, Polymer 4 was prepared as described above, now using the resultant Kunipia F dispersion prepared with either Disperbyk or with Anti-Terra, giving Polymer 7 and 8 respectively. To these polymers Kunipia F was post-added, using the resultant dispersion prepared with either Disperbyk or with Anti-terra, giving Example 7 and 8. Table 3 lists the relevant data.

Table 3

	Kunipia added by step 1 (wt%)	Kunipia added by step 2 (wt%)	Total amount of Kunipia added (wt%)	Solids content dispersion (%)	Viscosity (m.Pa.s.)	pH
Polymer 7	5.9	0	5.9	13.5	357	9.87
Example 7	5.9	5.9	11.8	11.2	280	9.80
Polymer 8	5.9	0	5.9	13.5	334	9.84
Example 8	5.9	5.9	11.8	11.2	81	9.73

Application of the polymer dispersions on a substrate

Polypropylene film (CDC-28, standard OPP grade (film thickness 28 μm) available from Treofan, corona treated by the supplier) was primed with polyethylene imine (Polymin P available from BASF, diluted to 0.5 wt% and applied with a dry film weight of 0.015 g/m²). The primer was applied by a RK Coater with a line speed of 10m/min and dried at 80 °C. Example 1 to 8 were applied onto the primed CDC-28 with a dry coat weight of 4.5 g/m² using a wire rod and dried 10 minutes at 80 °C.

Table 4 shows the O₂ permeability data for Examples 1-8 as measured under dry conditions. Example 1 was measured under dry as well as under wet conditions (85% RH). For further explanation of oxygen permeability, see below.

Table 4 Permeability data

Example	% Kunipia add. in- situ (s/s)	p cm ³ / m ² day atm	P2 cm ³ mm / (m ² day atm)	% Kunipia post- added (s/s)	Total amount of Kunipia F (%, s/s)	p cm ³ / m ² day atm	P2 cm ³ mm / (m ² day atm)	Δ
1	8.3	828	8.22	14.9	23.2	225 (336)*	1.19 (2.09)*	6.7 (4.5)*
2	2.0	1013	13.81	8.4	10.4	666	5.21	2.3
3	5.0	965	11.98	5.7	10.7	664	5.21	2.3
4	2.0	896	9.89	8.4	10.4	416	2.58	3.6
5	2.7	801	7.66	7.4	10.1	651	5.15	2.3
6	13.6	448	2.86	8.3	21.9	238	1.27	6.4
7	5.9	555	3.95	5.9	10.8	310 (443)*	1.75 (2.82)*	4.9 (3.4)*
8	5.9	626	4.8	5.9	10.8	363	2.15	4.2
PP based substrate	-	1513	-	-	-	-	-	-

Δ = Improvement in p is calculated against the PP-substrate ($p_{\text{PP}} / p_{\text{post-addition}}$)

* = @ 85% RH

From Table 4 it can be seen that by a two-step process compared to a one-step process an improvement in intrinsic oxygen barrier of the coating can be

reached of the respective factors: 6.9, 2.7, 2.3, 3.8, 1.5, 2.3, 2.3, 2.2. Also from Table 4 it can be seen that an additional reduction in O₂ permeability is obtained when Kunipia F is post-added. It can also be seen from Table 5 that when all Kunipia F was added by an in-situ process gelation took place already during the polymerization. Furthermore, it can be derived from the Table that the oxygen barrier performance is only slightly dependant on relative humidity. A low humidity- dependence of the barrier properties is a positive aspect as a large humidity- dependence of the water permeability (e.g. a factor > 3 between dry (0% RH) and wet conditions (85% RH)) is undesirable for many barrier applications.

Table 5 compares the viscosities of Examples 1-8 with in-situ and post-added Kunipia with the viscosities when all clay was introduced by the in-situ process only (as described in US 6,383,507).

Table 5 Viscosity

Example	Viscosity (m.Pa.s.) Before post addition	Solid content (%)	Viscosity (m.Pa.s.) after post addition	Solid content (%)	Viscosity all #
1	160	19.2	1092	11.2	Gel
2	47	20.0	604	15.4	Gel
3	366	20.0	974	16.7	Gel
4	168	20.0	489	15.4	Gel
5	278	20.0	432	17.6	Gel
6	257	11.6	257	6.8	> 1500
7	357	13.5	280	11.2	Gel
8	334	13.5	81	11.2	> 1500

= viscosity when all clay was added in-situ

As can be seen from Table 5, although the viscosity increased upon the post-addition of Kunipia F even when the solid content was reduced, the final viscosities were much lower compared to when the same amount of Kunipia F was all added only by the in-situ process, in which case all polymers formed a gel during the preparation.

Determination of permeabilities

Determination of the overall permeability ($\text{cm}^3 / \text{m}^2 \text{ day atm}$) of the two-layer system and the intrinsic permeability P_2 of the coating ($\text{cm}^3 \text{ mm} / \text{m}^2 \text{ day atm}$)

The overall oxygen permeability of the prepared two-layer samples was measured by a MOCON OX-TRAN 2/21 permeameter according to ASTM D3985 by exposing the films to a nitrogen environment on one side and an oxygen containing atmosphere at the other side of the films containing 21% oxygen to mimic atmospheric conditions. This leads to an oxygen partial pressure difference over the samples of 0.21 atm. The permeability tests were conducted under dry conditions at room temperature (23°C). The steady state oxygen permeability as measured under these conditions in $\text{cm}^3 / (\text{m}^2 \text{ day } 0.21 \text{ atm})$ is converted to an overall permeability in $\text{cm}^3 / (\text{m}^2 \text{ day atm})$ by simple multiplication by a factor $1/0.21$ in line with the general accepted Henry's law for oxygen solubility behavior.

The intrinsic oxygen permeability of the coating layer is estimated in the following way. In fact we are dealing here with a two layer system that can be regarded as a connection in a series fashion with each layer having its individual resistance for mass transport. The resistances for mass transport sum up in an additive way to give the resistance for mass transport for the total system.

The resistance for mass transport is given by the reciprocal permeability of the layer with permeability in $\text{cm}^3 / (\text{m}^2 \text{ day atm})$.

$$\frac{1}{P} = \frac{1}{P_1} + \frac{1}{P_2}$$

With:

- p: overall permeability in $\text{cm}^3 / (\text{m}^2 \text{ day atm})$ of the two-layer system
 p1: permeability in $\text{cm}^3 / (\text{m}^2 \text{ day atm})$ of the CDC-28 = $1513 \text{ cm}^3 / (\text{m}^2 \text{ day atm})$
 p2: permeability in $\text{cm}^3 / (\text{m}^2 \text{ day atm})$ of the coating.

The above equation can be converted to:

$$\frac{1}{P} = \frac{1}{P_1} + \frac{d}{P_2}$$

30

With:

d: thickness of the coating = $4.5 \cdot 10^{-6} \text{ m}$

P2: intrinsic permeability of the coating in $\text{cm}^3 \text{ mm} / (\text{m}^2 \text{ day atm})$.

So, by measuring p and p_1 , and knowing d , P_2 can be easily extracted.

CLAIMS

1. Process for the preparation of a polymer-clay nano-composite composition comprising at least the following steps:
 - 5 • optionally preparing a first clay mixture by mixing at least one clay with a clay suitable medium,
 - preparing a polymerization mixture of one or more monomers in a suitable polymerization medium,
 - 10 • combining the first clay mixture and/or at least one solid clay with the polymerization mixture and mixing them so as to obtain a polymerization-clay mixture,
 - polymerizing the one or more monomers in the polymerization-clay mixture until the desired characteristics for the polymer are reached after which the polymerization is stopped, so as to obtain a polymer,
 - 15 • optionally preparing a second clay mixture by mixing at least one clay with a clay suitable medium,
 - adding the second clay mixture and/or at least one solid clay to the polymer obtained in a previous step and mixing them so as to obtain a polymer-clay nano-composite composition A,
 - 20 • optionally separating the polymer-clay nano-composite from the rest of the polymer-clay nano-composite composition A.
2. Process for the preparation of a polymer-clay nano-composite composition comprising at least the following steps:
 - 25 A. optionally preparing a first clay mixture by mixing at least one clay with a clay suitable medium,
 - B. preparing a first polymerization mixture of one or more monomers in a suitable polymerization medium,
 - C. combining the first clay mixture and/or at least one solid clay with the first polymerization mixture and mixing them so as to obtain a first
 - 30 polymerization-clay mixture,
 - D. polymerizing the one or more monomers in the first polymerization-clay mixture until the desired characteristics for the first stage polymer are reached, after which the polymerization is stopped so as to obtain a first stage polymer,

- E. optionally preparing a further clay mixture by mixing at least one clay with a clay suitable medium,
- F. preparing a further polymerization mixture of one or more monomers in a suitable further polymerization medium,
- 5 G. adding the further polymerization mixture and the optional further clay mixture and/or at least further solid clay to the first stage polymer and mixing them so as to obtain a further polymer- clay mixture,
- H. polymerizing the one or more monomers in the further polymerization- clay mixture until the desired characteristics for the polymer are reached, after
- 10 which the polymerization is stopped so as to obtain a polymer-clay nano-composite composition B,
- I. optionally separating the polymer-clay nano-composite from the rest of the polymer-clay nano-composite composition B,
- J. optionally repeating the steps E-J.
- 15 3. Process according to claim 1 or 2 characterized in that the ratio of clay that is incorporated in the first mixture to the clay that is incorporated in the second mixture is between 10:1 and 1:10.
4. Process according to anyone of claims 1-3 characterized in that up to approximately 50wt% clay is incorporated in the polymer-clay nano-composite.
- 20 5. Polymer-clay nano-composite or polymer-clay nano-composite composition obtainable by the process of anyone of claim 1-4.
6. Substrate coated with a polymer-clay nano-composite of polymer-clay nano-composite composition according to claim 5.
7. Process to improve the barrier properties of a substrate comprising at least the
- 25 following steps:
- optionally pre-treating the substrate,
 - optionally mixing the polymer-clay nano-composite obtained by the process in anyone of claim 1-4 with a suitable polymer-clay nano-composite medium so as to obtain a polymer-clay nano-composite composition B,

30

 - applying the polymer-clay nano-composite composition B or the polymer-clay nano-composite composition A obtained in the process according to anyone of claim 1-4 onto the substrate,
 - optionally removing the polymer-clay nano-composite medium.

8. Substrate with improved barrier properties obtainable by the process according to claim 7.
9. Substrate coated with a polymer-clay nano-composite which coated substrate has an oxygen barrier that is a factor 2-10 better than the uncoated substrate.
- 5 10. Use of a polymer-clay nano-composite or polymer-clay nano-composite composition according to claim 5.
11. Use according to claim 10 to coat a substrate.
12. Use according to claim 11 for improving the barrier properties of a substrate.
13. Use of a substrate according to anyone of claim 6, 8-9 for packaging food,
10 perishables, medical instruments, electronic instruments or electronic parts.

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2009/054952

A. CLASSIFICATION OF SUBJECT MATTER

INV. C08F2/44

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)

C08F

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 practical, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2002/086908 A1 (CHOU CHUEN-SHYONG [US] ET AL) 4 July 2002 (2002-07-04) claims 1,3 paragraph [0100]	1-13
Y	HESHENG XIA AND MO SONG: "Intercalation and exfoliation behaviour of clay layers in branched polyol and polyurethane/clay nanocomposites" POLYMER INTERNATIONAL,, vol. 55, 1 January 2006 (2006-01-01), pages 229-235, XP007908758 table 2	1-13

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

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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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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2002086908 A1	04-07-2002	US 2005059769 A1	17-03-2005