

A Coating Suspension

Technical Field

- 5 The present invention relates to a coating suspension for high oxygen barrier coating, a process for making the coating suspension, and uses of the same.

Background Art

- 10 Ideal food packaging is always desired to preserve the nutritional value of food and keep them clean, fresh and fit for consumption over sufficiently long storage period. Proper food packaging also reduces energy consumption for storage and hence reduces carbon emission.

- 15 The barrier property of the packaging materials plays an important role in making sure that the product reaches the consumer in the best possible condition. Among the most important barrier properties are those against oxygen and moisture. Most foods require packaging with a high barrier to oxygen to help reduce oxidative degradation and fat rancidity. The need for packaging materials to exhibit barrier property to moisture is to keep the moisture content of the foods packaged at their best condition, which otherwise may lose or gain moisture during storage.
- 20 Some products such as potato chips and baked cookies that are manufactured with low moisture content need to remain dry to maintain their crispness, while other products such as pies and soft cheeses manufactured with high moisture content need to maintain the moisture content during storage with the help of packaging. A good combination of oxygen and moisture barrier is important for majority of foods, if not all.

- 25 Among the barrier materials available in the market, aluminium foil laminations and metalized plastic film are known to provide the highest barrier properties. A disadvantage of such materials is their high cost that makes them unsuitable for high-volume commodity product. Besides the cost, they are also clumsy and non-transparent: the foil layer is normally thicker than 1
- 30 millimetre in order to be free of pinholes that eliminate the transparency. However, transparency is also desirable for marketing purpose. Therefore, transparent plastics are currently employed in packaging and account for 37% of all global packaging sales on materials basis in 2010. It is expected to be the fastest growing packaging material up to 2015 with a predicted average annual growth rate of over 4%.

- 35 Plastic films such as Polyethylene terephthalate (PET), polypropylene (PP) and polyethylene (PE) are extensively used in packaging due to their low cost, strength and stiffness, transparent and flexibility properties. Despite having good mechanical strength and moldability properties, the barrier performance of commercially available plastic films in the market today is still relatively
- 40 poor, especially against oxygen, which cannot satisfy the crucial need for food packaging.

Therefore, there is a need to provide a coating suspension to overcome or at least ameliorate, one or more of the disadvantages described above, and to further improve the oxygen barrier performance.

Summary

There is provided an aqueous coating suspension that comprises:

- a) layered double hydroxide (LDH);
- b) at least one modifier; and
- c) a polymer matrix.

In an aspect, there is provided an aqueous coating suspension that comprises:

- a) layered double hydroxide (LDH);
- b) at least one modifier, wherein the modifier comprises a silane coupling agent selected from the group consisting of (3-aminopropyl)trimethoxysilane, (3-glycidopropyl)trimethoxysilane, and mixtures thereof; and
- c) a polymer matrix, wherein the polymer matrix comprises at least one polymer having a hydroxyl functional group and at least one polymer having a carboxyl functional group and wherein the weight ratio of the polymer having a hydroxyl functional group and the polymer having a carboxyl functional group is 9:1 to 2:1.

Advantageously, layered double hydroxide (LDH) with well-designed composition and structure could yield advanced functional materials for new applications or studies which need homogeneous materials with well-defined sizes and shapes. Further advantageously, the synthesized LDH may have features including high purity, tunable structure and morphology and mass production, as compared to natural sourced clay.

There is provided a process of preparing the coating suspension described herein, comprising the steps of:

- a. providing an aqueous suspension of layered double hydroxide (LDH); and
- b. contacting the layered double hydroxide (LDH) aqueous suspension with an aqueous solution of polymer having a hydroxyl functional group followed by an aqueous solution of polymer having a carboxyl functional group.

In another aspect, there is provided a process of preparing the coating suspension as defined above, comprising the steps of:

- a1) contacting an aqueous suspension of LDH with at least one modifier, wherein the at least one modifier is as defined above,
- a) providing an aqueous suspension of layered double hydroxide (LDH), and
- b) contacting the layered double hydroxides (LDHs) aqueous suspension with an aqueous solution of polymer having a hydroxyl functional group followed by an aqueous solution of polymer having a carboxyl functional group.

Advantageously, the aqueous solution of polymer having a hydroxyl functional group is mixed with positively charged LDH solution first to moderate the bonding strength between LDH and the polymer having a carboxyl functional group. Therefore, a stable gelatinous suspension can be produced without gel formation, and the suspension can be further applied onto substrates directly. As a result, the LDH/polymer barrier film with appropriate bonding strength show better oxygen barrier than that prepared from naturally sourced clay.

There is provided an aqueous coating suspension prepared by the process described herein.

There is provided a film formed comprising a substrate and a coating layer wherein the coating layer comprises a layered double hydroxide (LDH) and a polymer matrix, wherein the LDH has a hierarchical LDH structure that LDH platelet stacks onto the substrate layer by layer.

- 5 In another aspect, there is provided a film comprising a substrate and a coating layer wherein the coating layer comprises a layered double hydroxide (LDH) and a polymer matrix,
wherein the LDH is chemically coupled to the polymer matrix by a modifier or mixtures thereof to form strong interfacial bonding between the LDH and polymer matrix,
10 wherein the modifier comprises a silane coupling agent selected from the group consisting of (3-aminopropyl)trimethoxysilane, (3-glycidoxypentyl)trimethoxysilane, and mixtures thereof, and:
wherein the polymer matrix comprises at least one polymer having a hydroxyl functional group and at least one polymer having a carboxyl functional group and wherein the weight ratio of the polymer having a hydroxyl functional group and the polymer having a carboxyl functional group is 9:1 to 2:1,
15 and wherein the LDH has a hierarchical LDH structure wherein the LDH platelet stacks onto the substrate layer by layer.

In another aspect, there is provided a method for forming a film comprising the step of applying the coating suspension as described herein on a substrate.

- 20 During application, the modified LDH are aligned along the plastic substrate under shearing force to produce hierarchical LDH structure with high efficient tortuous path against gas molecules. The surface modification of LDH with silane is crucial for strong interfacial bonding between LDH and polymer matrix as well as that between LDH/polymer composite and plastic substrate for high oxygen
25 barrier.

In another aspect, there is provided use of the film as described herein as an oxygen barrier for making packaging films.

- 30 Advantageously, the coating suspension and film with layered double hydroxides (LDHs) is significantly better at preventing oxygen transmission than current compositions based on natural sourced clay due to the longer length of LDH and the strong bonding between the components of the LDH/polymer composite.

Definitions

The following words and terms used herein shall have the meaning indicated:

- 5 The term “chemically coupled”, “chemically coupling” and grammatical variants thereof, in the context of this specification, refers to the coupling of two or more chemical entities by way of a chemical bond. The term includes both a direct coupling where two or more chemical entities are bonded together by a chemical bond and indirect coupling where an intermediate entity forms a bond with one entity and another entity. For example, chemical coupling refers to the coupling between
10 silicate and the polymer matrix that occurs when a coupling agent forms chemical bonds with both the silicate and the polymer matrix. Hence, the silicate and polymer matrix are held together via the coupling agent.
- 15 The term “gelatinous suspension” is to be interpreted broadly to refer to a liquid composition whereby one of the constituents in the liquid composition is present in a particulate semisolid form in the Suspension.
- 20 The term “barrier layer” and “barrier film” as used herein refer to a layer and film of composite material which blocks or impedes gas migration.
- The word “substantially” does not exclude “completely” e.g. a composition which is “substantially free” from Y may be completely free from Y. Where necessary, the word “substantially” may be omitted from the definition of the invention.
- 25 Unless specified otherwise, the terms “comprising” and “comprise”, and grammatical variants thereof, are intended to represent “open” or “inclusive” language such that they include recited elements but also permit inclusion of additional, unrecited elements.
- 30 As used herein, the term “about”, in the context of concentrations of components of the formulations, typically means +/- 5% of the stated value, more typically +/- 4% of the stated value, more typically +/- 3% of the stated value, more typically, +/- 2% of the stated value, even more typically +/- 1% of the stated value, and even more typically +/- 0.5% of the stated value.
- 35 Throughout this disclosure, certain embodiments may be disclosed in a range format. It should be understood that the description in range format is merely for convenience and brevity and should not be construed as an inflexible limitation on the scope of the disclosed ranges. Accordingly, the description of a range should be considered to have specifically disclosed all the possible sub-ranges as well as individual numerical values within that range. For example, description of a
40 range such as from 1 to 6 should be considered to have specifically disclosed sub-ranges such as from 1 to 3, from 1 to 4, from 1 to 5, from 2 to 4, from 2 to 6, from 3 to 6 etc., as well as individual numbers within that range, for example, 1, 2, 3, 4, 5, and 6. This applies regardless of the breadth of the range.
- 45 Certain embodiments may also be described broadly and generically herein. Each of the narrower species and subgeneric groupings falling within the generic disclosure also form part of the disclosure. This includes the generic description of the embodiments with a proviso or negative

limitation removing any subject matter from the genus, regardless of whether or not the excised material is specifically recited herein.

Detailed Disclosure of Embodiments

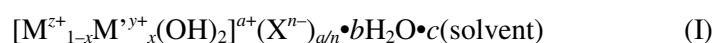
Exemplary, non-limiting embodiments of an aqueous coating suspension will now be disclosed.

The present disclosure relates to an aqueous coating suspension that comprises:

- a. layered double hydroxide (LDH);
- d) at least one modifier; and
- e) a polymer matrix.

Layered double hydroxides (LDHs) are a class of synthetic or natural two dimensional nanostructured layered materials with two kinds of metallic cations in the main layers and interlayer domains containing anionic species. Advantageously, layered double hydroxide (LDH) materials with well-designed composition and structure could yield advanced functional materials for new applications or studies which need homogeneous materials with well-defined sizes and shapes.

The layered double hydroxide (LDH) has a chemical formula according to formula (I) shown below:



wherein

M and M' are charged metal cations and M is different from M';

z may be 1 or 2;

y may be 3 or 4;

$0 < x < 0.9$, preferably $0.1 \leq x \leq 0.5$

$b = 0-10$

$c = 0-10$

X is an anion

n is the charge on the anion X, n may be preferably selected from 1, 2, 3, 4, or 5.

$a > 0$ and $a = z(1-x) + xy - 2$ and ;

solvent is solvent with a hydrogen bond donor or acceptor function.

In the layered double hydroxide of formula (I), x has a value according to the expression $0.1 < x < 0.5$. Suitably, x has a value according to the expression $0.18 < x < 0.5$. More suitably, x has a value according to the expression $0.18 < x < 0.4$.

In the LDH formula, b has a value according to the expression $0 < b \leq 7.5$. Suitably, b has a value according to the expression $0 < b \leq 5$. More suitably, b has a value according to the expression $0 < b \leq 3$. Even more suitably, b has a value according to the expression $0 < b \leq 1$ (e.g. $0.2 < b \leq 0.95$).

In the LDH formula, c has a value according to the expression $0 \leq c \leq 5$. Suitably, c has a value according to the expression $0 \leq c \leq 1$. More suitably, c has a value according to the expression $0 \leq c \leq 0.01$. Even more suitably, c has a value according to the expression $0 \leq c \leq 0.000005$. Most suitably, c has a value according to the expression $c = 0$.

The LDH may have a volatile content which is presented as $b + c$ in the range of 0 - 1, preferably 0 - 0.6. The volatile content refers to the amount of volatile substance where the volatile substance are water, solvent or a mixture thereof. The volatile content is measured by Karl fisher titration technique for water content and gas chromatography/mass spectrometry GC/MS headspace technique for solvent content.

The LDH contains positively charged metal hydroxide layers with charge balancing X anions located between the layers.

5 The LDH may comprise a first metal M and a second metal M'.

It is preferred that the first metal M and the second metal M' are selected from different metal cations.

10 Preferably, the molar ratio of the first metal M to the second metal M' is in the range from 1:1 to 10:1, more preferably from 2:1 to 7:1, and most preferably from 2:1 to 5:1.

The first metal M is at least one monovalent metal cation, one divalent metal cation or a combination thereof. Preferably, the first metal M is at least one divalent metal cation.

15 Furthermore, the second metal M' is at least one trivalent metal cation, one tetravalent metal cation or a combination thereof. Preferably, the second metal M' is at least one trivalent metal cation.

20 The first metal M may be selected from lithium, zinc, magnesium, iron, calcium, tin, nickel, copper, cobalt and combinations thereof, preferably from calcium, magnesium, zinc, copper, nickel and combinations thereof, more preferably from magnesium, zinc and combinations thereof. In one embodiment, the first metal M comprises magnesium, preferably consists of magnesium.

25 The second metal M' may be selected from aluminium, iron, gallium, indium, yttrium, cobalt, manganese, chromium, titanium, vanadium, lanthanum, tin, zirconium and combinations thereof, preferably from aluminium, gallium, indium, iron, cobalt, tin, zirconium and combinations thereof. In one embodiment, the second metal M' comprises, preferably consists of, aluminium.

In one embodiment, the first metal M comprises, preferably consists of magnesium, and the second metal M' comprises, preferably consists of aluminium.

30 In an embodiment, a layered double hydroxide of formula (I) is provided which is a Zn/Al, Mg/Al, ZnMg/Al, Ni/Ti, Mg/Fe, Ca/Al, Ni/Al or Cu/Al layered double hydroxide, preferably is Mg/Al layered double hydroxide.

35 In an embodiment, a layered double hydroxide of formula (I) is provided with the formula $M_qM'-A$, wherein $1.8 \leq q \leq 5$, and preferably wherein $2 \leq q \leq 4$.

In an embodiment, a layered double hydroxide of formula (I) is provided which is a Mg_4Al-CO_3 layered double hydroxide.

40 In an embodiment, a layered double hydroxide of formula (I) is provided which is a Mg_3Al-CO_3 layered double hydroxide.

45 In an embodiment, a layered double hydroxide of formula (I) is provided which is a Mg_2Al-CO_3 layered double hydroxide.

The anion in the LDH may be otherwise any appropriate anion, organic or inorganic, for example halide (e.g., chloride, bromide), inorganic oxyanions (e.g. $X_mO_n(OH)_p^{-q}$; $m = 1-5$; $n = 2-10$; $p = 0-4$, $q = 1-5$; $X = B, C, N, S, P$: e.g. carbonate, bicarbonate, hydrogenphosphate, dihydrogenphosphate, nitrite, borate, nitrate, phosphate, sulphate), anionic surfactants (such as sodium dodecyl sulfate, fatty acid salts or sodium stearate), anionic chromophores, and/or anionic UV absorbers, for example 4-hydroxy-3-methoxybenzoic acid, 2-hydroxy-4-methoxybenzophenone-5-sulfonic acid (HMBA), 4-hydroxy-3-methoxy-cinnamic acid, p-aminobenzoic acid and/or urocanic acid.

In one specific embodiment, X is selected from carbonate, hydroxide, fluoride, chloride, bromide, iodide, sulphate, nitrate and phosphate. In a preferred embodiment, the X is selected from carbonate and nitrate. In a first most preferred embodiment, X is carbonate. In a second most preferred embodiment, the X is nitrate.

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The solvent with a hydrogen bond donor or acceptor function is, in any amount, miscible with water. Hydrogen bond donor groups may include R-OH, R-NH₂, R₂NH, whereas hydrogen bond acceptor groups may include ROR, R₂C=O, RNO₂, R₂NO, R₃N, ROH, RCF₃ [R is hydrocarbyl group]. Exemplary solvents include ethyl acetate, acetone, acetonitrile, dimethylformamide, dimethylsulfoxide, dioxane, ethanol, m-cresol, o-cresol, p-cresol, methanol, n-propanol, isopropanol, n-butanol, sec-butanol, n-pentanol, n-hexanol, cyclohexanol, diethyl ether, diisopropyl ether, di-n-butyl ether, methyl tert-butyl ether (MTBE), tert-amyl methyl ether, cyclopentyl methyl ether, anisole, butyl carbitol acetate, cyclohexanone, methyl ethyl ketone (MEK), methyl isobutyl ketone (MIBK), methyl isoamyl ketone, methyl n-amyl ketone, isophorone, isobutyraldehyde, furfural, methyl formate, methyl acetate, isopropyl acetate, n-propyl acetate, isobutyl acetate, n-butyl acetate, n-amyl acetate, n-hexyl acetate, methyl amyl acetate, methoxypropyl acetate, 2-ethoxyethyl acetate, 2-butoxyethyl acetate, n-butyl propionate, n-pentyl propionate, triethylamine, 2-nitropropane, aniline, N,N-dimethylaniline, nitromethane, tetrahydrofuran, and mixtures of two or more thereof. Preferably, the solvent is ethanol or acetone.

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The LDH may be a plate-like or sheet-like structure. The LDHs may have an aspect ratio in the range from about 3 to about 1000, about 5 to about 1000, about 10 to about 1000, about 15 to about 1000, about 20 to about 1000, about 25 to about 1000, about 30 to about 1000, about 40 to about 1000, about 50 to about 1000, about 70 to about 1000, about 100 to about 1000, about 300 to about 1000, about 500 to about 1000, about 700 to about 1000, about 900 to about 1000, about 3 to about 900, about 3 to about 700, about 3 to about 500, about 3 to about 300, about 3 to about 100, about 3 to about 70, about 3 to about 50, about 3 to about 40, about 3 to about 30, about 3 to about 25, about 3 to about 20, about 3 to about 10 or about 3 to about 5.

The LDHs may have a lateral size of the platelet in the range of about 50 nm to about 1000 nm, about 100 nm to about 1000 nm, about 200 nm to about 1000 nm, about 300 nm to about 1000 nm, about 400 nm to about 1000 nm, about 500 nm to about 1000 nm, about 700 nm to about 1000 nm, about 800 nm to about 1000 nm, about 900 nm to about 1000 nm, about 50 nm to about 100 nm, about 50 nm to about 200 nm, about 50 nm to about 300 nm, about 50 nm to about 400 nm, about 50 nm to about 500 nm, about 50 nm to about 700 nm, about 50 nm to about 800 nm, about 300 nm to about 500 nm, about 300 nm to about 600 nm, about 300 nm to about 700 nm, about 300 nm to about 800 nm, or about 300 nm to about 900 nm.

The LDHs may have a thickness of the platelet in the range of about 1 nm to about 200 nm, about 5 nm to about 200 nm, about 10 nm to about 200 nm, about 20 nm to about 200 nm, about 30 nm to about 200 nm, about 50 nm to about 200 nm, about 70 nm to about 200 nm, about 100 nm to about 200 nm, about 120 nm to about 200 nm, about 150 nm to about 200 nm, about 170 nm to about 200 nm, about 1 nm to about 170 nm, about 1 nm to about 150 nm, about 1 nm to about 120 nm, about 1 nm to about 100 nm, about 1 nm to about 70 nm, about 1 nm to about 50 nm, about 1 nm to about 30 nm, about 1 nm to about 20 nm, about 1 nm to about 10 nm, about 1 nm to about 5 nm, about 100 nm to about 120 nm, about 100 nm to about 150 nm, or about 100 nm to about 170 nm.

LDH with high aspect ratio and lateral size of 300 nm or longer may be used for high oxygen barrier application.

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The LDH may have a Zeta potential of about +10 mV to about +40 mV, about +12 mV to about +40, about +15 mV to about +40 mV, about +17 mV to about +40 mV, about +20 mV to about +40 mV, about +25 mV to about +40 mV, about +30 mV to about +40 mV, about +35 mV to about +40 mV, about +10 mV to about +35 mV, about +10 mV to about +30 mV, about +10 mV to about +25 mV,

about +10 mV to about +20 mV, about +10 mV to about +17 mV, about +10 mV to about +15 mV, about +10 mV to about +12 mV, about +15 mV to about +35 mV or about +17 mV to about +35 mV. The interfacial interaction between LDH and the polymer having a carboxyl functional group is stronger with the increase of the Zeta potential of LDH. However, gelation is always formed if the Zeta potential of LDH is too high, such as LDH with Zeta potential of +30 mV and above.

Advantageously, the synthesized LDH may have features including high purity, tunable structure and morphology and mass production, as compared to natural sourced clay.

The layered double hydroxide (LDH) content in the coating suspension may be in the range of about 2.5 wt% to about 50 wt%, about 5 wt% to about 50 wt%, about 10 wt% to about 50 wt%, about 15 wt% to about 50 wt%, about 20 wt% to about 50 wt%, about 30 wt% to about 50 wt%, about 40 wt% to about 50 wt%, about 2.5 wt% to about 40 wt%, about 2.5 wt% to about 30 wt%, about 2.5 wt% to about 20 wt%, about 2.5 wt% to about 15 wt%, about 2.5 wt% to about 10 wt%, about 2.5 wt% to about 5 wt%, about 10 wt% to about 30 wt%, about 10 wt% to about 20 wt%, or about 20 wt% to about 30 wt% based on total solid weight of coating suspension.

The modifier content may be in the range of about 2 to about 30%, about 2 to about 25%, about 2 to about 20%, about 2 to about 15%, about 2 to about 10%, about 2 to about 5%, about 5 to about 30%, about 5 to about 25%, about 5 to about 20%, about 10 to about 20%, about 10 to about 30%, about 15 to about 30%, about 20 to about 30% or about 25 to about 30% based on total weight of LDH.

The modifier may be a silane coupling agent, a fatty acid or an organic phosphonic acid.

The silane coupling agent may be glycidoxysilanes, amino silanes or mixtures thereof.

The glycidoxysilanes may be a glycidoxyalkylalkoxysilane compound. The glycidoxyalkylalkoxysilane compound may be selected from the group consisting of glycidoxymethyltrimethoxysilane, glycidoxymethyltriethoxysilane, glycidoxymethyltripropoxysilane, glycidoxyethyltrimethoxysilane, glycidoxyethyltriethoxysilane, glycidoxyethyltripropoxysilane, glycidoxypropyltrimethoxysilane, glycidoxypropyltriethoxysilane, glycidoxypropyltripropoxysilane, glycidoxypropyltri(methoxyethoxy)silane, glycidoxypropylmethyldimethoxysilane, glycidoxypropylmethyldiethoxysilane, glycidoxypropylmethyldibutoxysilane, glycidoxypropylmethyldiisopropenoxysilane, glycidoxypropyldimethylethoxysilane, glycidoxypropyldimethylpropoxysilane, glycidoxypropylmethyldiisopropenoxysilane, glycidoxypropylbis(trimethylsiloxy)methylsilane, glycidoxybutyltrimethoxysilane, hydrolyzates thereof, and mixtures thereof. Additional exemplary glycidoxysilanes may be obtained from US 5,115,069.

The amino silanes may be an aminoalkylalkoxysilane compound. The aminoalkylalkoxysilane compound may be selected from the group consisting of aminomethyltrimethoxysilane, aminomethyltriethoxysilane, aminomethyltripropoxysilane, aminoethyltrimethoxysilane, aminoethyltriethoxysilane, aminoethyltripropoxysilane, aminopropyltrimethoxysilane, aminopropyltriethoxysilane, aminopropyltripropoxysilane, aminopropyltrimethoxyethoxysilane, aminopropylmethyldimethoxysilane, aminopropylmethyldiethoxysilane, aminopropylmethyldibutoxysilane, aminopropylmethyldiisopropenoxysilane, aminopropyldimethylethoxysilane, aminopropyldimethylpropoxysilane, aminopropylmethyldiisopropenoxysilane, aminopropylbis(trimethylsiloxy)methylsilane, aminobutyltrimethoxysilane, or mixtures thereof.

The silane may be a mixture of (3-aminopropyl)trimethoxysilane and (3-glycidoxypropyl)trimethoxysilane at a weight ratio selected from the range of about 1:9 to about 9:1, preferably at a weight ratio selected from the range 1:3 to 3:1, and more preferably at a weight ratio selected from the range 2:3 to 3:2.

The silane coupling agent content may be in the range of about 1 to about 10%, about 2 to about 10%, about 3 to about 10%, about 4 to about 10%, about 5 to about 10%, about 6 to about 10%, about 7 to about 10%, about 8 to about 10%, about 9 to about 10%, about 1 to about 9%, about 1 to about 8%, about 1 to about 7%, about 1 to about 6%, about 1 to about 5%, about 1 to about 4%, about 1 to about 3%, about 1 to about 2%, about 2 to about 3% or about 4 to about 6% based on total weight of LDH.

The modifier may be a saturated or unsaturated fatty acid selected from the group consisting of stearic acid, palmitic acid, oleic acid, limoleic acid, linolenic acid, and combinations thereof. The modifier may be an organic phosphonic acid selected from aminotris(methylensphosphonic acid), ethylenediamine tetra(methylene phosphonic acid), and combinations thereof. The modifier may be stearic acid.

The fatty acid or organic phosphonic acid modifier content may be in the range of about 2 to about 20%, about 2 to about 15%, about 2 to about 10%, about 2 to about 5%, about 5 to about 20%, about 5 to about 15%, about 5 to about 10%, about 10 to about 20%, or about 15 to about 20% based on total weight of LDH.

The polymer matrix may be comprised of at least one polymer having a hydroxyl functional group and at least one polymer having a carboxyl functional group. The polymer matrix may be comprised of a combination of at least one polymer having a hydroxyl functional group and at least one polymer having a carboxyl functional group.

The polymer having a hydroxyl functional group may be selected from the group consisting of polyvinyl alcohol (PVA), polyvinyl alcohol derivatives, polyvinyl alcohol copolymers, starch, starch derivatives, chitosan, chitosan derivatives, cellulose, cellulose derivatives such as cellulose ether and ester derivatives, gums, arabinans, galactans, galactomannans, proteins, various other polysaccharides and mixtures thereof. The polyvinyl alcohol polymer comprises mainly monomer units of vinyl alcohol. The polyvinyl alcohol copolymer may comprise poly (ethylene-co-vinyl alcohol) (EVOH) of varying vinyl alcohol content. The polymer having a hydroxyl functional group may be a water-soluble synthetic polymer. It has then the idealized formula $[\text{CH}_2\text{CH}(\text{OH})]_n$. The polymer having a hydroxyl functional group may be polyvinyl alcohol (PVA).

The polymer having a hydroxyl functional group may have a molecular weight (MW) in the range of about 1,000 to about 100,000 g/mol, about 3,000 to about 100,000 g/mol, about 5,000 to about 100,000 g/mol, about 10,000 to about 100,000 g/mol, about 20,000 to about 100,000 g/mol, about 40,000 to about 100,000 g/mol, about 60,000 to about 100,000 g/mol, about 80,000 to about 100,000 g/mol, about 1,000 to about 80,000 g/mol, about 1,000 to about 60,000 g/mol, about 1,000 to about 40,000 g/mol, about 1,000 to about 20,000 g/mol, about 1,000 to about 10,000 g/mol, about 1,000 to about 5,000 g/mol, or about 1,000 to about 3,000 g/mol. The hydrolysis of the polymer having a hydroxyl functional group may be 98% and above. In general, the polymer having a hydroxyl functional group with high hydrolysis percentage shows strong bonding with the polymer having a carboxyl functional group and LDH as well as better barrier performance.

The content of the polymer having a hydroxyl functional group in the coating suspension may be in the range of about 1 wt% to about 15 wt%, about 1 wt% to about 12 wt%, about 1 wt% to about 10 wt%, about 1 wt% to about 7 wt%, about 1 wt% to about 5 wt%, about 4 wt% to about 8 wt%, about 3 wt% to about 9 wt%, about 3 wt% to about 7 wt%, about 2 wt% to about 8 wt%, about 2 wt% to about 15 wt%, about 5 wt% to about 15 wt%, about 8 wt% to about 15 wt%, about 10 wt% to about 15 wt%, or about 12 wt% to about 15 wt% based on the aqueous coating suspension.

The PVA content in the aqueous coating suspension is in a range of 1 to 15 wt% , 1 to 12 wt%, 1 to 10 wt%, 1 to 7 wt%, 1 to 5 wt%, 4 to 8 wt%, 3 to 9 wt%, 3 to 7 wt%, 2 to 8 wt%, 2 to 15 wt%, 5 to 15 wt%, 8 to 15 wt%, 10 to 15 wt%, or 12 to 15 wt% based on the aqueous coating suspension.

The polymer having a carboxyl functional group may be selected from the group consisting of polycarboxylic acid, polycarboxylic acid derivatives, polycarboxylic acid copolymer and mixtures thereof. The polymer having a carboxyl functional group may be polyacrylic acid (PAA).

The content of the polymer having a carboxyl functional group in the coating suspension may be in the range of about 0.1 wt% to about 10 wt%, about 0.1 wt% to about 8 wt%, about 0.1 wt% to about 6 wt%, about 0.1 wt% to about 4 wt%, about 0.1 wt% to about 2 wt%, about 0.1 wt% to about 1 wt%, about 0.5 wt% to about 2 wt%, about 1 wt% to about 10 wt%, about 1 wt% to about 5 wt%, about 1 wt% to about 3 wt%, about 2 wt% to about 10 wt%, about 4 wt% to about 10 wt%, about 6 wt% to about 10 wt%, or about 8 wt% to about 10 wt% based on the aqueous coating suspension.

The PAA content in the aqueous coating suspension is in a range of 0.1 to 10 wt%, 0.1 to 8 wt%, 0.1 to 6 wt%, 0.1 to 4 wt%, 0.1 to 2 wt%, 0.1 to 1 wt%, 0.5 to 2 wt%, 1 to 10 wt%, 1 to 5 wt%, 1 to 3 wt%, 2 to 10 wt%, 4 to 10 wt%, 6 to 10 wt%, or 8 to 10 wt% based on the aqueous coating suspension.

The polymer having a carboxyl functional group may have a molecular weight (MW) of about 200,000 to about 600,000 g/mol, about 300,000 to about 600,000 g/mol, about 400,000 to about 600,000 g/mol, about 500,000 to about 600,000 g/mol, about 200,000 to about 500,000 g/mol, about 200,000 to about 400,000 g/mol, or about 200,000 to about 300,000 g/mol.

The weight ratio of the polymer having a hydroxyl functional group and the polymer having a carboxyl functional group may be selected in the range of about 9:1 to about 2:1, about 9:1 to about 4:1, about 9:1 to about 8:1, about 8:1 to about 2:1, about 7:1 to about 2:1, about 6:1 to about 2:1, about 5:1 to about 2:1, or about 4:1 to about 2:1. The ratio of the polymer having a hydroxyl functional group and the polymer having a carboxyl functional group is preferably in the range of about 5:1 to 2:1.

The final solid LDH/polymer concentration in the coating suspension may be in the range of about 1 to about 10%, about 1 to about 9, about 1 to about 8%, about 1 to about 7%, about 1 to about 6%, about 1 to about 5%, about 1 to about 4%, about 1 to about 3%, about 1 to about 2%, about 2 to about 10%, about 3 to about 10%, about 4 to about 10%, about 5 to about 10%, about 6 to about 10%, about 7 to about 10%, about 8 to about 10% or about 9 to about 10. The concentration of LDH/polymer may be calculated by measuring the weight change of a part of the coating suspension before and after complete drying.

Advantageously, silane(s) modified LDH may be chemically coupled to the polymer matrix by a silane coupling agent or mixtures thereof to form strong interfacial bonding between the LDH and polymer matrix, which is crucial for better oxygen barrier. Upon heating, the glycidoxo functional

group from the glycidoxysilanes will react with the carboxyl functional group from the polymer having a carboxyl functional group and the hydroxyl functional group from the polymer having a hydroxyl functional group to form chemical bonds.

Further advantageously, the positively charged layered double hydroxides (LDHs) may have strong electrostatic interaction with a negatively charged polymer in the polymer matrix. The negatively charged polymer may be the polymer with the carboxyl functional group. The protonated amino group from amino silanes could form electrostatic interaction with the deprotonated carboxyl functional group from the polymer having a carboxyl functional group. Therefore, the coating suspension may have significant technical advantages when applied onto a substrate for film formation whereby the coated substrate may have high barrier performance to air.

The coating suspension may be a gelatinous suspension of LDHs/polymer(s), wherein the layered double hydroxides (LDHs) are present in the gelatinous suspension. The term "gelatinous suspension" is to be interpreted broadly to refer to a liquid composition whereby one of the constituents in the liquid composition is present in a particulate semisolid form in the suspension.

Exemplary, non-limiting embodiments of a process of preparing the coating suspension will now be disclosed.

The process of preparing the coating suspension described herein comprises the steps of:

- a) providing an aqueous suspension of layered double hydroxide (LDH), and
- b) contacting the layered double hydroxide (LDH) aqueous suspension with an aqueous solution of polymer having a hydroxyl functional group followed by an aqueous solution of polymer having a carboxyl functional group.

The LDH may firstly be exfoliated into water under homogenization or high speed stirring for a period of time, such as from 4 hours to overnight. Advantageously, it may not be necessary to add additional reagents, such as a small volume of acetic acid, to promote exfoliation of LDH sheets in the suspension, since LDH with strong positive surface charge can be exfoliated into water easier than natural sourced clay.

The process may further comprise the step of, before step a), the step a1) of contacting an aqueous suspension of LDH with at least one modifier.

The modifier may be a fatty acid or a phosphonic acid. The modified LDH may be made by dispersing the LDH in an aqueous solution and adding a fatty acid or a phosphonic acid slowly or dropwise with efficient stirring.

Advantageously, the fatty acid or phosphonic acid modifier can neutralize the strong positive surface charge of LDH to reduce its entanglement with polyanions such as the polymer having a carboxyl functional group.

The modifier may be a silane or a mixture of silanes. Thus, the modified LDHs may be regarded as silane-modified LDHs. Modified LDH may be made by dispersing the LDH in an aqueous solution and adding a silane at a slow injection speed under high homogenization speed. The flow rate of the injection of the silane may be in the range of about 0.1 to about 3.0 mL/min, about 0.3 to about 3.0 mL/min, about 0.5 to about 3.0 mL/min, about 1.0 to about 3.0 mL/min, about 2.0 to about 3.0 mL/min, about 0.1 to about 2.0 mL/min, about 0.1 to about 1.0 mL/min, about 0.1 to about 0.5 mL/min, or about 0.1 to about 0.3 mL/min. The homogenization speed may be in the range of about 5,000 to about 20,000 rpm, or about 15,000 to about 20,000 rpm of a suitable disperser. A typical lab

disperser, such as an IKA® T 18 digital ULTRA-TURRAX®, can be used with an adequate high speed setting.

Advantageously, such silane modification with LDH will improve LDH dispersion into polymer solution to form uniform and stable coating suspension. It may strengthen the bonding by crosslinking the alkoxy reactive group of the silane with the LDH, where the epoxy reactive group cross-links with the polymer in the polymer matrix. Addition of amino silanes and glycidoxysilanes may aid to further improve the bonding strength and adhesion to the polymer and substrate, thereby forming a strong composite material.

A heating step may be involved after the injection of the modifier. In this heating step, an elevated temperature may be applied. Typical temperatures may be about 35°C to 90°C, about 45°C to 90°C, about 55°C to 90°C, about 65°C to 90°C, about 75°C to 90°C, about 85°C to 90°C, about 35°C to 85°C, about 35°C to 75°C, about 35°C to 65°C, about 35°C to 55°C, about 35°C to 45°C or about 45°C to 85°C. The heating step may be for about 2 to 8 hours, preferably about 3 to 6 hours, more preferably about 4 to 5 hours under vigorous stirring.

Advantageously, the suitable hydrophilicity of acid neutralized LDH can be achieved through tuning the acid neutralization degree in order to incorporate the acid neutralized LDH into aqueous polymer solution to produce stable and uniform solution. The acid neutralized LDH must be modified with silane further to produce LDH/polymer coating suspension with high oxygen barrier, which is due to the uniform dispersion of acid-silane-LDH in the polymer and its strong bonding with the polymer. Therefore the acid modification would be followed by silane modification for optimal end results.

In one embodiment, the process of preparing the coating suspension comprise the steps of:

- a) providing an aqueous suspension of layered double hydroxide (LDH),
- b) contacting the aqueous suspension of LDH with a modifier, preferable contacting with the fatty acid or phosphonic acid modifier followed by silane and/or mixture of silane,
- c) contacting the aqueous suspension of modified LDH with an aqueous solution of polymer having a hydroxyl functional group followed by an aqueous solution of polymer having a carboxyl functional group.

In a preferred embodiment, the process of preparing the coating suspension comprise the steps of:

- a) providing an aqueous suspension of layered double hydroxide (LDH),
- b) contacting the aqueous suspension of LDH with the fatty acid, preferably stearic acid to form an aqueous suspension of fatty acid modified LDH (acid-LDH)
- c) contacting the acid-LDH with amino silanes, preferably APTMS followed by glycidoxysilanes, preferably GPTMS to form an aqueous suspension of fatty acid and silane modified LDH (silane-acid-LDH)
- d) contacting the silane-acid-LDH with an aqueous solution of polymer having a hydroxyl functional group, preferably PVA followed by an aqueous solution of polymer having a carboxyl functional group, preferably PAA.

The process for the preparation of LDH/polymer water-based coating suspension may comprise the steps of preparation of silanes modified LDH and mixing silanes modified LDH homogeneously into polymer aqueous solutions under homogenization or high speed stirring. The homogenization speed may be in the range of about 5,000 to about 20,000 rpm, about 10,000 to about 20,000 rpm, or about 15,000 to about 20,000 rpm of a suitable disperser. The coating suspension is then allowed to further homogenize for a sufficient time in the range of about 5 to about 30 minutes, or about 10 to about 20 minutes, to produce the coating suspension.

Due to the strong positive surface charge of LDH, modified LDH is preferably mixed with polyvinyl alcohol first and then with polyacrylic acid sequentially to produce uniform and stable coating suspension.

Advantageously, the aqueous solution of polymer having a hydroxyl functional group is mixed with positively charged LDH solution first to moderate the bonding strength between LDH and the polymer having a carboxyl functional group. Therefore, a stable gelatinous suspension can be produced without gel formation, and the suspension can be further applied onto substrates directly. As a result, the LDH/polymer barrier film with appropriate bonding strength show better oxygen barrier than that prepared from naturally sourced clay. Further advantageously, no phase separation is observed in the coating suspension for at least 12 hours, resulting in the possibility of using the coating suspension to form a uniform coating on a substrate. If the aqueous solution of polymer having a carboxyl functional group is mixed with the positively charged LDH solution first, the ionic bond is too strong and gel will be formed, which cannot be further applied onto any substrate.

The present disclosure also relates to an aqueous coating suspension prepared by the above preparation method.

The present disclosure also relates to a film comprising a substrate and a coating layer wherein the coating layer comprises a layered double hydroxide (LDH) and a polymer matrix, wherein the LDH has a hierarchical LDH structure whereby the LDH platelet stacks onto the substrate layer by layer.

Advantageously, the film may have an oxygen transmission rate of 0.1 cc/(m².day) or less, preferably 0.05 cc/(m².day) or less, and more preferably 0.02 cc/(m².day) or less.

The oxygen transmission rate of the LDH/(PVA-PAA) barrier film could be as low as 0.01 cc/(m².day) when the aspect ratio of the LDH is 50 and above. The oxygen transmission rate of barrier film could be at most 0.1 cc/(m².day). Advantageous, the coating suspension and film is significantly better at preventing oxygen transmission than the compositions with natural sourced clay due to the longer length of LDH and the strong bonding between the components of the LDH/polymer composite.

The thickness of the coating layer may be about 0.15 to 3.5 μm, about 0.2 to 3.5 μm, about 0.5 to 3.5 μm, about 1.0 to 3.5 μm, about 2.0 to 3.5 μm, about 3.0 to 3.5 μm, about 0.15 to 3.0 μm, about 0.15 to 2.0 μm, about 0.15 to 1.0 μm, about 0.15 to 0.5 μm, or about 0.15 to 0.2 μm.

The substrate may be a plastic film. The plastic film may be a polyamide (PA) film, a polycarbonate (PC) film, a polyester (PES) film, a polyethylene (PE) film, a polypropylene (PP) film, a polystyrene (PS) film, a polyurethanes (PU) film, a polyvinyl chloride (PVC) film, a polyvinylidene chloride (PVDC) film, a acrylonitrile butadiene styrene (ABS) film, or a polyethylene terephthalate (PET) film. The plastic film may preferably be a polyethylene terephthalate (PET) film.

The film may further comprise a protective layer on top of the coating layer. The protective layer may be a polyalkylene layer. The protective layer may be a polypropylene (PP) layer or a linear low-density polyethylene (LLDPE) layer.

The transparency of the film can be influenced by the concentration of composites and the thickness of the barrier film. Process optimization to produce a thin barrier film with a thickness of less than 3.5 μm, or a thickness which is below 1 μm may be used in packaging to fulfil the requirements of low material usage and low film thickness combined with excellent transparency. The film may have a light transmission rate of more than 65%.

The present disclosure also relates to a method for forming a film on a substrate comprising the step of applying a coating suspension described herein on the substrate.

The method may comprise the following steps: a) applying the coating suspension described herein on the substrate under a shearing force to form a barrier layer thereon and b) drying the formed barrier layer on the substrate.

The method may comprise the following steps: a) applying the coating suspension described herein on the substrate under a shearing force to form a barrier layer thereon, b) drying the formed barrier layer on the substrate, and c) coating the obtained bi-layer substrate with an adhesive and laminating with a protective layer. The substrate may be a plastic film.

The substrate which is coated with the suspension may be a plastic film. The plastic film may be a polyamide (PA) film, a polycarbonate (PC) film, a polyester (PES) film, a polyethylene (PE) film, a polypropylene (PP) film, a polystyrene (PS) film, a polyurethanes (PU) film, a polyvinyl chloride (PVC) film, a polyvinylidene chloride (PVDC) film, a acrylonitrile butadiene styrene (ABS) film, or a polyethylene terephthalate (PET) film. The plastic film may preferably be a polyethylene terephthalate (PET) film. Before drying, the thickness of the coated barrier layer may be about 5 to about 50 μm . The shearing force applied during the applying step may involve the use of blade coater using a film applicator to form a barrier layer thereon.

Advantageously, the LDH sheets are homogeneously dispersed in the composites and aligned along the substrate plane by employing the shearing force during the application, and may not affect the optical properties of the barrier layer. The polymeric materials will also be intercalated between the LDH sheets as a binder to produce hierarchical LDH/polymer structure, which creates high efficient tortuous path against gas molecules cross the barrier layer to show high barrier. The alignment of LDH sheets along the plastic substrate was confirmed by cross-section TEM images of the barrier film.

The applied composites layer on the plastic substrate is then dried by air flash at room temperature, followed by a heating step which may involve vacuum drying at about 40 to 80 $^{\circ}\text{C}$ or hot air drying. The interfacial bonding between modified LDH and polymer may be enhanced during the drying process under heating.

The method may further comprise the step of coating a protective layer onto the coating layer. At least another protective layer may be laminated onto the coating layer by using an adhesive as a binder in order to improve the adhesion between the layer (to be laminated) and the already coated substrate. The applied adhesive/plastic bilayer is dried by air flash at room temperature or hot air drying. A heating step may be undertaken when the (modified LDH/polymer composite)/plastic bilayer film is compressed together with the adhesive/plastic to form a plastic/(modified LDH/polymer composites)/plastic trilayer film which can be covered by additional layers. The temperature used during the heating step may be in the range of about 60 to 140 $^{\circ}\text{C}$ depending on the plastic substrate used. The temperature applied may be about 130 $^{\circ}\text{C}$ for a polyethylene terephthalate substrate. The heating step may be a laminating step. It is preferable to apply pressure during the lamination process.

The present disclosure also relates to use of the film as described herein as an oxygen barrier for making packaging films

With the platelet like structure similar to that of natural sourced clay, the LDH could be incorporated into polymer matrix to form a torturous path against oxygen and moisture for improving the barrier performance of polymer matrix.

Advantageously, in comparison to natural sourced clay, the synthetic LDH is more uniform in size and longer in length which are good for high gas barrier because of the higher efficient tortuous path.

At the same time, the composition of LDH is controllable with less impurity which is safe for food packaging application.

Brief Description of Drawings

5

The accompanying drawings illustrate a disclosed embodiment and serves to explain the principles of the disclosed embodiment. It is to be understood, however, that the drawings are designed for purposes of illustration only, and not as a definition of the limits of the invention.

Fig. 1

[Fig. 1] shows a schematic structure of LDH with positively charged layers (**100**) and interlayer anions (**200**).

Fig. 2

15 [Fig. 2] shows TEM image of Mg_2Al LDH (Zeta potential $+16.4 \pm 1.1$ mV) with length of about 400 nm.

Fig. 3

20 [Fig. 3] shows the XPS spectra of LDH (Zeta potential +31.1 mV), LDH/PAA and LDH-SA where the appearance of new shoulder on the left demonstrated the strong bonding between LDH and PAA or SA.

Fig. 4

25 [Fig. 4] shows The FTIR spectra of LDH (Zeta potential +31.1 mV), PAA, LDH/PAA and LDH/SA where the observation of new aliphatic chain peak between 2750 and 3000 cm^{-1} and free CO_3^{2-} peak in LDH-12.5%SA demonstrates the formation of interfacial bonding between SA and LDH in LDH/SA.

Fig. 5

30 [Fig. 5] shows XRD results showing no significant changes in the characteristics peaks of LDH (Zeta potential +31.1 mV) before and after SA modification.

Fig. 6

35 [Fig. 6] shows coating suspensions by adding PAA first followed by PVA (sequence of addition: LDH/ H_2O + silane + PAA + PVA) (A), and by adding PVA first followed by PAA (sequence of addition: LDH/ H_2O + silane + PVA + PAA) (B).

Fig. 7

40 [Fig. 7] shows UV-Vis data of the PET/LDH-PVA-PAA/LLDPE film.

Fig. 8

45 [Fig. 8] shows transparency of the PET/LDH-PVA-PAA/LLDPE film: (A) no film on the logo; (B) with LDH/(PVA-PAA) coated PET film on the logo.

Fig. 9

[Fig. 9] shows structure of the LDH/(PVA/PAA) composite coating by TEM. The arrow shows the direction of plastic substrate plane.

5 **Examples**

Non-limiting examples of the invention and a comparative example will be further described in greater detail by reference to specific Examples, which should not be construed as in any way limiting the scope of the invention.

10 **Materials and Methods**

In the examples described below, unless otherwise indicated, all temperatures in the following description are in degrees Celsius and all parts and percentages are by weight, unless indicated otherwise. Reagents useful for synthesizing compounds may be purchased from commercial suppliers as mentioned in the examples.

Polyacrylic acid (PAA) was purchased from Polysciences Taiwan (Polysciences Asia Pacific, Inc) and polyvinyl alcohol (PVA) was purchased from Scientific Hub Services Pte Ltd, a local distributor in Singapore of Wako Pure Chemical Industries LTD Japan. Both (3-aminopropyl)trimethoxysilane (APTMS) and (3-glycidoxypopyl)trimethoxysilane (GPTMS) were bought from Sigma-Aldrich Singapore. Stearic acid was purchased from Fisher scientific, a local distributor in Singapore of Acros organics.

25 **Test Methods**

Oxygen Transmission Rate

Oxygen permeability of nanocomposites coated PET film was measured by using Mocon oxygen permeability OX-TRAN Model 2/21 according to ASTM D3985. Each film was placed on a stainless steel mask with an open testing area of 50 cm². Oxygen permeability measurements were conducted at 23°C (1 atm) and 0% relative humidity by placing coated surface of films to the oxygen rich side.

Cross-section TEM Observation of LDH/(PVA-PAA) Barrier Film

The LDH/(PVA-PAA) (with 5 wt% silane) suspension was coated onto PET substrate with wet thickness of 15 µm. The film is cut with a sharp blade and embedded into epoxy to cure overnight. TEM specimen is then obtained using microtoming. TEM is done using JEOL 2100.

40 **Example 1: Preparation of silane modified LDH (silane-LDH)**

Fig. 1 shows a schematic structure of LDH with positively charged layers (**100**) and interlayer anions (**200**) and Fig. 2 shows a TEM image of Mg₂Al LDH with length of about 400 nm. 7.5 g of LDH (Zeta potential +17 mV) was dispersed into 192.5 g of Deionised (DI) water and allowed to stir at 600 rpm overnight. 146.05 µl of 3-aminopropyltrimethoxysilane was first slowly injected into the LDH suspension under homogenization at 14000 rpm for 5 minutes, followed by injecting 210.28 µl of (3-glycidoxypopyl)trimethoxysilane under homogenization at 14000 rpm for 10

minutes. LDH suspension (mixture of LDH and silane) was then heated at 50°C for 6 hours at high speed to produce silane modified LDH suspension of 3.75 wt%.

Example 2: Preparation of stearic acid modified LDH (stearic acid-LDH)

18.75 g of LDH (Zeta potential +31.1 mV) was dispersed into 50 g of deionised (DI) water for 30 minutes before 500 g of ethanol (EtOH) was added into the suspension. The suspension was stirred for at least 3 hours. The achieved suspension had a solid content of 3.3 wt% and was used as a masterbatch suspension. 120 g of the LDH-water-ethanol mixture was heated at 65 °C in oil bath for at least 30 minutes. A 7.5wt% stearic acid (SA) solution was prepared with 0.29 g of stearic acid solid dissolved in a mixture of 7.82 g EtOH and 0.78 g water at 65 °C (oil bath). The heated and fully dissolved SA solution was added into the heated LDH-water-ethanol dropwise under homogenization at 8500 rpm for 10 minutes. The solution was heated at 65 °C for 4 hours. The suspension was then centrifuged and washed with EtOH thrice, followed by water twice. Centrifuging was done at 6000-8000 rpm for 5 minutes. The washed LDH-SA was then dispersed into water where the total solid content was 3.75 wt%. This is under the assumption that there is no loss in LDH after the washing process. The suspensions were prepared as per Table 1, below.

Table 1. Stearic acid modification of LDH

LDH-water-EtOH (g)	Stearic acid to LDH	Stearic acid amount (g)	Ethanol (g)	Water (g)
120	5%	0.20	5.21	0.52
120	7.5%	0.29	7.82	0.78
120	10%	0.39	10.42	1.04
120	12.5%	0.49	13.03	1.3

The surface charge density of LDH is determined by LDH composition and its Zeta potential could be +30 mV or above. Strong surface charged LDH always entangles with polyanions such as PAA together to be precipitated or gelled from their solution due to the strong ionic bonding. The strong ionic bonding between LDH and PAA or Stearic acid is confirmed by XPS study.

Fig. 3 is the XPS results of LDH with Zeta potential of +31.1 mV and its mixture with PAA or Stearic acid, which confirms the strong bonding between LDH and PAA or SA, due to the interaction between the COOH of PAA or SA and Mg and Al cations of LDH. Therefore, SA was applied to neutralize LDH to reduce the entanglement between LDH and PAA to produce stable LDH/(PVA-PAA) coating suspension with gelation time longer than 12 hours. The neutralization degree was optimized to produce LDH with suitable hydrophilicity to be dispersed into polymer aqueous solution uniformly. The FTIR spectra of LDH, PAA, LDH/PAA and LDH/SA are shown in Fig. 4 where the observation of new aliphatic chain peak between 2750 and 3000 cm⁻¹ and free CO₃²⁻ peak in LDH-12.5%SA demonstrates the formation of interfacial bonding between SA and LDH in LDH/SA. Furthermore, XRD spectra (Fig. 5) shows that there are no significant changes in the characteristic peaks of LDH before and after SA treatment, which indicates that the crystalline structure of LDH is not destroyed during SA treatment.

Example 3: Preparation of silane-stearic acid-LDH

142.4 μ l of 3-aminopropyltrimethoxysilane was first slowly injected into 65g of stearic acid-LDH suspension (as prepared in Example 2) under homogenization at 8000 rpm for 5 minutes, followed by injecting 91.1 μ l of (3-glycidioxypropyl)trimethoxysilane under homogenization at 8000 rpm for 10mins. The achieved LDH –SA-Silane suspension was then heated at 65 °C for 6 hours to produce silane-stearic acid-LDH suspension.

Example 4: Preparation of PAA Solution

50 g of PAA was dissolved in 500 g of DI water under stirring at room temperature to produce a solution with total solid content of 9.09 wt%.

Example 5: Preparation of PVA Solution

75 g of PVA was dissolved in 425 g of DI water under stirring at 90°C to produce a solution with total solid content of 15 wt%. In addition, 50 g of PVA was dissolved in 450 g of deionized water under stirring at 90 °C to produce a solution with total solid content of 10 wt%.

Example 6: Preparation of silane-LDH/(PVA-PAA) Coating Suspension

16.73 g of PVA solution was added into 20 g of silane-LDH suspension prepared in Example 1 slowly under homogenization at 14000 rpm. 7.87 g of DI water is added to the mixture to achieve the desired solid content. 5.4 g of PAA solution was then added into the mixed suspension under homogenization at 14000 rpm. The mixture was then homogenized for 15 mins to produce LDH/(PVA-PAA) coating suspension with a total solid content of 7.5 wt % and LDH content of 20 wt% against to the PVA and PAA. The sequence of adding PVA and PAA is important as shown in Fig.6. By adding PAA first followed by PVA, a clear separation can be observed due to gel formation as shown in Fig. 6A, which cannot be further applied onto other substrates. By adding PVA first followed by PAA, a stable gelatinous suspension as shown in Fig. 6B can be produced which can be further applied onto substrates directly.

The solid content, LDH content and PVA-PAA ratio of the LDH/(PVA-PAA) coating suspension can be varied according to Table 1 below to achieve individual stable suspension following the preparation reported in Example 4. 20 wt% PVA solution was used in the examples of 8 wt% solid content.

Solid content (wt%)	PVA/PAA ratio	LDH in solid content (wt%)	Modified LDH suspension (3.75wt%) (g)	PVA solution 15wt%/20wt%* (g)	Additional water	PAA solution 9.09wt%
6.7	5.1:1	10	10	18.82	21.08	6.07
		20	20	16.73	13.84	5.40
		30	30	14.64	6.61	4.72
7.5		10	10	18.82	15.11	6.07
		20	20	16.73	7.87	5.40
		30	30	14.64	0.64	4.72
8		10	10	14.12*	16.69	6.07
		20	20	12.55*	8.93	5.40

		30	30	10.98*	1.17	4.72
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Table 1. Formula for preparation of silane-LDH/(PVA-PAA) coating suspension with various solid content, LDH solid content at a fixed PVA-PAA ratio

5 Solid content is calculated as solid content of silane-LDH, PVA and PAA divided by the weight of LDH suspension, PVA solution, PAA solution and additional water, and multiplied by 100 to give the unit of wt%.

10 LDH in solid content refers to the solid weight percentage of LDH in PVA, PAA and LDH, and is calculated as solid weight of LDH divided by the solid weight of PVA, PAA and LDH, and multiplied by 100 to give the unit of wt%.

PVA/PAA ratio is calculated as the ratio of solid weight of PVA against solid weight of PAA.

15 **Example 7: Preparation of silane-stearic acid-LDH/(PVA-PAA) Coating Suspension**

20 59.22 g of 10 wt% PVA solution was added into 20 g silane-stearic acid-LDH suspension prepared in Example 3 slowly under stirring at 900 rpm followed by stirring for 10 minutes. 11.67 g of deionised water was added to the mixture to achieve the desired solid content. 9.11 g of 9.09 wt% PAA solution was then added into the mixed suspension under stirring at 1000 rpm. The mixture was then stirred for 15 minutes at 1000 rpm to produce silane-stearic acid-LDH /(PVA-PAA) coating suspension with a total solid content of 7.5 wt % .

25 **Example 8: Preparation of LDH/(PVA-PAA) Composites Film**

30 Silane-LDH/(PVA-PAA) coating suspensions obtained from Example 6 were blade coated onto a PET film by using a bird-type film applicator at the coating speed of 50 mm/second followed by air drying at room temperature and vacuum drying at 60°C. Before drying, the thickness of gelatinous coating suspension is 5 to 50 µm on the PET film. After drying, the thickness of the coated composites barrier layer will be about 0.25 to 2.5 µm.

35 Silane-stearic acid-LDH/(PVA-PAA) coating suspensions obtained from Example 7 were blade coated onto a PET film by using a conventional applier at the coating speed of 50 m/minute followed by air drying at room temperature and vacuum drying at 60 °C.

40 The obtained PET coated silane-LDH/(PVA-PAA) films were then laminated with linear low-density polyethylene (LLDPE) film using laminator (GBC 3500 Pro Series) to produce laminated PET/(silane-LDH/(PVA-PAA))/LLDPE film at a laminating temperature of between 90 to 110°C with polyurethane as adhesive. The UV-Vis spectra of the PET/(silane-LDH/(PVA-PAA))/LLDPE film is shown in Fig. 7. A good transparency of the film can be achieved as observed in Fig. 8.

45 **Comparative Example 1: Preparation film using naturally sourced clay as compared to LDH**

50 To prepare the barrier film using naturally sourced clay, natural source clay was dispersed into DI water at a solid concentration of 3.75 wt% and stirred for at least 5 hrs. The clay suspension was then sonicated using the ultrasonic bath for 30 minutes and the suspension was stirred overnight. Acetic acid was added to the clay suspension and stirred overnight at room temperature. The clay suspension was treated with 5% silanes (APTMS and GPTMS at ratio of 2:3) and the silane treated clay

suspension was heated at 50°C for 6 hours and stirred overnight at room temperature. PAA and PVA were added into the silane modified clay suspension, with clay concentration at 30% of the whole coating suspension. The naturally source clay/(PVA-PAA) composites film with lamination was then prepared with the procedure in Example 8.

The oxygen transmission rate of the prepared barrier films was measured by using Mocon oxygen permeability OX-TRAN Model 2/21 according to ASTM D3985. The oxygen transmission rate of LDH/(PVA-PAA) barrier film was as low as 0.01 cc/(m².day) when the length of LDH is 400nm or above. With the similar coating thickness and composition, the oxygen transmission rate of naturally sourced clay/(PVA-PAA) composite was about 0.2 cc/(m².day). Therefore, the oxygen transmission rate of LDH/(PVA-PAA) composite was significantly improved by using LDH instead of naturally source clay because the length of LDH was longer than that of naturally source clay and the bonding was stronger between the components of the LDH/(PVA-PAA) composite. A TEM image comparison has been shown in Fig. 9 to show the structure difference of a LDH/(PVA-PAA) composite and a naturally sourced clay/(PVA-PAA) composite. The naturally sourced clay in Figure 9B shows non-uniform clay sheet with smaller size in comparison to LDH. Larger lateral size and the hierarchical structure of LDH in Figure 9A are critical to achieve the advantage of better oxygen barrier property.

The oxygen transmission rate could be as low as 0.04 cc/(m².day) when LDH (Zeta potential +31.1 mV) was modified with varying SA% and silane ratio. Table 2 below shows the oxygen transmission rate of PET/mod-LDH/ (PVA-PAA) modified with various SA% concentration and silane ratio.

Table 2. The OTR of PET films coated with selected suspensions

LDH	Silane Ratio	PAA	Total solid content	OTR cc/(m ² .day)
LDH – 7.5% SA	2:3	0.75	7.5	0.06
LDH – 7.5% SA	3:2	0.75	7.5	0.09
LDH – 10% SA	2:3	0.75	7.5	0.04

Industrial Applicability

The present technology could be used to reduce the transmission of oxygen to the substrates such as plastics. The polymer composite suspensions may find a multiple number of applications in the manufacturing of barrier films for plastic films of packaging. For example, the methods as defined above may be used to manufacture packaging films with good barrier property. A good barrier film against oxygen is important to protect the produces packaged from fast oxidation and deterioration.

It will be apparent that various other modifications and adaptations of the invention are available to the person skilled in the art after reading the foregoing disclosure without departing from the spirit and scope of the invention and it is intended that all such modifications and adaptations come within the scope of the appended claims.

Claims

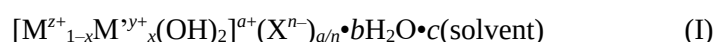
1. An aqueous coating suspension that comprises:

a) layered double hydroxide (LDH);

b) at least one modifier, wherein the modifier comprises a silane coupling agent selected from the group consisting of (3-aminopropyl)trimethoxysilane, (3-glycidopropyl)trimethoxysilane, and mixtures thereof; and

c) a polymer matrix, wherein the polymer matrix comprises at least one polymer having a hydroxyl functional group and at least one polymer having a carboxyl functional group and wherein the weight ratio of the polymer having a hydroxyl functional group and the polymer having a carboxyl functional group is 9:1 to 2:1.

2. The aqueous coating suspension according to claim 1, wherein the LDH has a chemical formula according to formula (I) shown below:



wherein

M and M' are charged metal cations and M is different from M';

z is 1 or 2;

y is 3 or 4;

$0 < x < 0.9$, preferably $0.1 \leq x \leq 0.5$

b = 0-10

c = 0-10

X is an anion

n is the charge on the anion X,

$a > 0$ and $a = z(1-x) + xy - 2$ and ;

solvent is solvent with a hydrogen bond donor or acceptor function.

3. The aqueous coating suspension according to claim 2, wherein M is selected from the group consisting of lithium, zinc, magnesium, iron, calcium, tin, nickel, copper, cobalt and combinations thereof, and M is preferably magnesium, and

wherein M' is selected from the group consisting of aluminium, iron, gallium, indium, yttrium, cobalt, manganese, chromium, titanium, vanadium, lanthanum, tin, zirconium and combinations thereof, and M' is preferably aluminium, and

wherein X is selected from the group consisting of carbonate, hydroxide, fluoride, chloride, bromide, iodide, sulphate, nitrate and phosphate and combinations thereof, preferably carbonate.

4. The aqueous coating suspension according to any one of the preceding claims, wherein the LDH has a platelet morphology, wherein the LDH has an aspect ratio in the range of 3 – 1000 and/or wherein the lateral size of the platelet is in the range of 50 – 1000 nm and/or wherein the thickness of the platelet is in the range of 1 – 200 nm and/or wherein the LDH content is in the range of 2.5 to 50 wt% based on total solid weight of coating suspension.

5. The aqueous coating suspension according to any one of the preceding claims, wherein the modifier comprises a fatty acid and/or an organic phosphonic acid, and/or wherein the modifier content is in the range of 2 to 30% based on total weight of LDH.

6. The aqueous coating suspension according to claim 5, wherein the silane is a mixture of (3-aminopropyl)trimethoxysilane and (3-glycidopropyl)trimethoxysilane at a weight ratio selected from the range of 1:9 to 9:1.

7. The aqueous coating suspension according to claim 5, wherein the fatty acid is a saturated or unsaturated fatty acid selected from the group consisting of stearic acid, palmitic acid, oleic acid, limoleic acid, linolenic acid and combinations thereof.
- 5 8. The aqueous coating suspension according to claim 5, wherein the organic phosphonic acid is selected from the group consisting of aminotris(methylensphosphonic acid), ethylenediamine tetra(methylene phosphonic acid), and combination thereof.
- 10 9. The aqueous coating suspension according to claim 1, wherein the content of the polymer having a hydroxyl functional group in the coating suspension is in a range of 1 wt% to 15 wt% based on the aqueous coating suspension and/or wherein the content of the polymer having a carboxyl functional group in the coating suspension is in a range of 0.1 wt% to 10 wt% based on the whole suspension.
- 15 10. The aqueous coating suspension according to claim 9, wherein the polymer having a hydroxyl functional group is selected from the group consisting of a polyvinyl alcohol (PVA), polyvinyl alcohol derivatives, polyvinyl alcohol copolymers, starch, starch derivatives, chitosan, chitosan derivatives, cellulose, cellulose derivatives, cellulose ether, cellulose ester derivatives, gums, arabinans, galactans, galactomannans, proteins, and mixtures thereof and wherein the polymer having a carboxyl functional group is selected from the group consisting of a polyacrylic acid (PAA),
 - 20 polycarboxylic acid, polycarboxylic acid derivatives, polycarboxylic acid copolymer and mixtures thereof.
- 25 11. The aqueous coating suspension according to any one of the preceding claims, wherein the polymer matrix comprises a polyvinyl alcohol (PVA) polymer and a polyacrylic acid (PAA).
- 30 12. A process of preparing the coating suspension of any one of claims 1 to 11, comprising the steps of:
 - a1) contacting an aqueous suspension of LDH with at least one modifier, wherein the at least one modifier is as defined in claim 1,
 - a) providing an aqueous suspension of layered double hydroxide (LDH), and
 - b) contacting the layered double hydroxides (LDHs) aqueous suspension with an aqueous solution of polymer having a hydroxyl functional group followed by an aqueous solution of polymer having a carboxyl functional group.
- 35 13. The process according to claim 12, wherein the silane coupling agent is added into the aqueous suspension of LDH at an injection rate of 0.1 to 3.0 mL/min and at a homogenization speed of 5,000 to 20,000 rpm.
- 40 14. A film comprising a substrate and a coating layer wherein the coating layer comprises a layered double hydroxide (LDH) and a polymer matrix,
 - wherein the LDH is chemically coupled to the polymer matrix by a modifier or mixtures thereof to form strong interfacial bonding between the LDH and polymer matrix,
 - wherein the modifier comprises a silane coupling agent selected from the group consisting of (3-aminopropyl)trimethoxysilane, (3-glycidoxypentyl)trimethoxysilane, and mixtures thereof, and:
 - 45 wherein the polymer matrix comprises at least one polymer having a hydroxyl functional group and at least one polymer having a carboxyl functional group and wherein the weight ratio of the polymer having a hydroxyl functional group and the polymer having a carboxyl functional group is 9:1 to 2:1,
 - and wherein the LDH has a hierarchical LDH structure wherein the LDH platelet stacks onto
 - 50 the substrate layer by layer.
15. The film according to claim 14, wherein the modifier comprises a fatty acid and/or an organic phosphonic acid

- 16.. The film according to claim 15, wherein the fatty acid is a saturated or unsaturated fatty acid selected from the group consisting of stearic acid, palmitic acid, oleic acid, limoleic acid, linolenic acid, and combinations thereof, and the organic phosphonic acid is selected from the group consisting of aminotris(methylensphosphonic acid), ethylenediamine tetra(methylene phosphonic acid), and combinations thereof.
17. The film according to claim 14, wherein the film has an oxygen transmission rate of 0.1 cc/(m².day) or less.
18. The film according to claim 14, wherein the film has an oxygen transmission rate of 0.05 cc/(m².day) or less.
19. The film according to claim 14, wherein the film has an oxygen transmission rate of 0.02 cc/(m².day) or less.
20. The film according to any one of claims 14 to 19, wherein the thickness of the coating layer is 0.15 to 3.5 μ m.
21. The film according to any one of claims 14 to 20, wherein the substrate is a plastic film.
22. The film according to any one of claims 14 to 21, further comprising a protective layer on top of the coating layer.
23. The film according to any one of claims 14 to 22, wherein the film has a light transmission rate of more than 65%.
24. A method for forming a film comprising the step of applying the coating suspension according to any one of claims 1 to 11 on a substrate.
25. The method according to claim 24, wherein the method comprises the steps of: a) applying the suspension according to any one of claims 1 to 11 on the substrate under a shearing force to form a barrier layer, and b) drying the formed barrier layer on the substrate.
26. The method according to claim 24 or 25, further comprising the step of coating a protective layer onto the coating layer.
27. Use of the film according to any one of claims 14 to 23 as an oxygen barrier for making packaging films.