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(54) Title: MODIFIED PHYLLOSILICATE

(57) Abstract: Polymer nanocomposite comprising: a) a polylactic polymer; and b) a modified phyllosilicate composition comprising a modifying agent which is hexadecyl trimethyl ammonium cations which are intercalated between the layers of the phyllosilicate, its preparation process, as well as the modified phyllosilicate composition. The polymer nanocomposite is particularly useful for packaging, particularly food and drink packaging.

Modified phyllosilicate

The present invention relates to the modified phyllosilicate composition comprising a mixture of modifying agents, its preparation process and its uses.

BACKGROUND ART

It is well known in the art the preparation of modified phyllosilicates. Thus, under appropriate conditions an organic compound containing a cation can react by ion exchange with a phyllosilicate containing a negative layer lattice and exchangeable cations to form the modified phyllosilicate.

The modified materials are used at relatively high temperature in different application, for example the production of food packaging. These materials at high temperature can be unstable.

The effect of a mixture of modifying agents results on the thermal stability of the modified phyllosilicate.

Accordingly, the patent application EP1787918 describes a biodegradable polyester resin reinforced by a modified phyllosilicate. The phyllosilicate is substituted with ammonium, pyridinium, imidazolium, or phosphonium ions. Examples of ammonium ions include tetraethylammonium, octadecyltrimethylammonium, and dimethyldioctadecylammonium among other ions. The modified phyllosilicate describes in this patent application presents one type of modifying agent.

Thus, from what is known in the art, it is derived that the development of a modified phyllosilicates comprising a mixture of modifying agents with improved thermal properties is still of great interest.

SUMMARY OF THE INVENTION

Inventors have found that the modified phyllosilicate compositions comprising hexadecyltrimethyl ammonium cations and acetylcholine or choline are more stable at high temperatures than the phyllosilicate compositions comprising only hexadecyltrimethyl ammonium cations.

Thus, this modified phyllosilicate composition can be obtained at higher temperatures since no degradation of phyllosilicate compositions occurs which have the advantages of higher yields.

Therefore an aspect of the present invention relates to a modified phyllosilicate composition comprising a modifying agent which is hexadecyl trimethyl ammonium cations which are intercalated between the layers of the phyllosilicate and an additional modifying agent selected from the group consisting in acetylcholine and choline.

The silicate used in the invention belongs to the family of phyllosilicates, preferably smectite group. These compounds are characterized by their swelling properties and high cation-exchange capacities.

Another aspect of the present invention relates to a process for the production of a modified phyllosillicate as defined above, that is a phyllosilicate comprising a modifying agent which is hexadecyl trimethyl ammonium cations which are intercalated between the layers of the phyllosilicate and optionally an additional modifying agent which is acetylcholine or choline, the process comprising (a) dispersing the phyllosillicate in water and an C_1-C_{10} alcohol; (b) applying ultrasonic wave; (c) optionally adding choline salt or acetylcholine salt (d) adding hexadecyl trimethyl ammonium salt; (e) maintaining the mixture of step (d) at a temperature comprised between 20ºC and 120ºC; (f) isolating the compound obtained in step (d), wherein the step a), b), c), and d) can be carried out in any order.

The incorporation of a modified phyllosilicate composition of the invention to a polymer results in a polymer nanocomposite showing improved thermal resistance.

Therefore, another aspect of the present invention relates to the use of the modified phyllosilicate of the invention as a reinforcing agent of polymers.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 shows a thermogravimetric analysis up to 700ºC performed over the modified phyllosilicates.

FIG. 2 shows the young Modulus (GPa), (white column) and the elongation at break (mm), (black column) of different samples.

FIG. 3 shows the young Modulus (GPa), (white column) and the elongation at break (mm), (black column) of different samples.

FIG. 4 shows a plot of the heat flow versus temperature of different samples.

DETAILED DESCRIPTION OF THE INVENTION

As mentioned above, an aspect of the present invention relates to a modified phyllosilicate compositions comprising hexadecyltrimethyl ammonium cations and acetylcholine or choline.

The term “phyllosilicates” as used herein, refers to layered silicates in which the SiO_4 tetrahedra are linked together in two dimensional sheets and are condensed with layers of AlO_6 or MgO octahedra in the ratio 2:1 or 1:1. The negatively charged layers attract positive cations (e.g. Na^+, K^+, Ca^{2+}, Mg^{2+}.) which can hold the layers together. Non limiting examples phyllosilicate which may be used within the scope of the present invention are sodium montmorillonite, magnesium montmorillonite, calcium montmorillonite. In a preferred embodiment, the phyllosilicate is sodium montmorillonite.

The term “modified phyllosilicates” as used herein, refers to phyllosilicates wherein the positive cations (e.g. Na^+, K^+, Ca^{2+}, Mg^{2+}), are exchanged by ion exchange reactions with alkylammonium cations as modifying agents. Particularly, the modified phyllosilicate of the present invention comprises hexadecyl trimethyl ammonium and, optionally acetylcholine or choline cations, as modifying agents.

These modifiers are added in excess to the cation exchange capacity (CEC) of the phyllosilicate and it was established a value of 0.5-10 times the CEC as the optimum. The modification of a phyllosilicate with a mixture of modifiers simultaneously, provokes a favourable exchange with hexadecyl trimethyl ammonium versus choline or acetylcholine. For this reason, for the preparation of these modified phyllosilicate with a mixture of modifiers, it has been firstly performed the exchange with choline or acetylcholine a low concentration (0.1 – 1 CEC), and afterwards the exchange with the hexadecyl trimethyl ammonium was carried out (0.4 – 9.9 CEC). Therefore in a more preferred embodiment in nanocomposite with a mixture of modifiers, the amount of acetylcholine or choline is 0.20-0.75 meq/100g the value of the phyllosilicate CEC and the amount of hexadecyl trimethyl ammonium cation is 5.25-5.80 meq/100g the value of the phyllosilicate CEC. Therefore in another more preferred embodiment in nanocomposite with a mixture of modifiers, the amount of acetylcholine or choline is 0.25-0.50 meq/100g the value of the phyllosilicate CEC and the amount of hexadecyl trimethyl ammonium cation is 5.55-5.75 meq/100g the value of the phyllosilicate CEC.

As mentioned above, the modified phyllosilicate of the present invention, that is a phyllosilicate comprising a modifying agent which is hexadecyl trimethyl ammonium cations which are intercalated between the layers of the phyllosilicate and optionally an additional modifying agent which is acetylcholine or choline, can be prepared by a process comprising (a) dispersing the phyllosillicate in water and an C_1-C_{10} alcohol; (b) applying ultrasonic wave; (c) optionally adding choline salt or acetylcholine salt (d) adding hexadecyl trimethyl ammonium salt; (e) maintaining the mixture of step (d) at a temperature comprised between 20ºC and 120ºC; (f) isolating the compound obtained in step (d), wherein the step a), b), c), and d) can be carried out in any order.

In a preferred embodiment the phyllosilicate is dispersed in water and ethanol.

In a preferred embodiment, the choline salt added is choline halide. In a more preferred embodiment the choline salt adding is choline chloride.

In a preferred embodiment, the acetylcholine salt added is acetylcholine halide. In a more preferred embodiment the acetylcholine salt added is acetylcholine chloride.

In a preferred embodiment the hexadecyl trimethyl ammonium salt added is hexadecyl trimethyl ammonium halide. In a more preferred embodiment the hexadecyl trimethyl ammonium salt added is hexadecyl trimethyl ammonium bromide.

In a preferred embodiment the optionally addition of choline salt or acetylcholine salt and the addition of hexadecyl trimethyl ammonium salt is carried out slowly.

In a preferred embodiment the mixture of step (d) is maintained at a temperature comprised between 20ºC and 90ºC. In another preferred embodiment the mixture of step (d) is maintained at a temperature comprised between 50ºC and 90ºC. In a more preferred embodiment the mixture of step (d) is maintained at a temperature comprised between 65ºC and 75ºC.

In a preferred embodiment the isolating step f) comprises purifying of the modified phyllosilicate prepared. In a more preferred embodiment the phyllosilicate is purified with a solution of water:ethanol, in particular, the solution is added to the modified phyllosilicate, and the mixture is maintained under stirring at a temperature comprised between 50ºC-90ºC . The product is filtered and the conductivity of the mother liqueours is measured. This process is repeated until the mother liqueours have a conductivity below 5-30 µS/cm.

In a more preferred embodiment the isolating step comprises a drying step of the phyllosilicate after the purification. The drying step is carried out at a temperature comprised between 70ºC-90ºC. It can be carried out in a conventional oven, by lyophilisation or by atomization. Generally, the drying process last at least 12 hours. After the drying step, the phyllosilicate can be milled, and sieved. Generally it is sieved to a particle size below 25 microns.

As mentioned above the modified phyllosilicate of the invention can be used in the reinforcement of polymers. Preferably in the reinforcement of polymers used in food packaging. Preferably in the reinforcement of polyethylenes (PE), polypropylenes (PP), poly(ethylene-vinyl acetates (EVA), polystyrenes (PS), polyvinyl chlorides (PVC), ionomers (I), polyethylene terephthalates (PET), polyvinyl acetates (PVAc), polycarbonates (PC), polyamides (PA), polyvinyl alcohols (PVOH), polyvinylidene chlorides (PVDC). More preferably PP, PE, or PET.

The incorporation of a modified phyllosilicate of the invention to a biodegradable polymer, in particular polylactic polymer (PLA) results in a polymer nanocomposite showing not only improved mechanical properties but also improved barrier properties and thermal resistance. The fact that the polymer nanocomposite shows excellent barrier properties is advantageous on the one hand, for its use for storage of aqueous drinks (e.g. water, juice, milk) since the lost of water vapour through the wall of the bottles is minimized. On the other hand, it is also advantageous for its use for food storage. Food containers must present a good barrier property against the diffusion of oxygen into the container, to avoid the spoliation of the food products caused by the presence of oxygen therein. In addition, the polymer nanocomposite of the present invention shows excellent mechanical strength and less rigidity which is an advantage for packaging long term storage, avoiding the polymer nanocomposite deformation and cracking.

Therefore, a polymer nanocomposite comprising a polylactic polymer and a modified phyllosilicate composition comprising a modifying agent which is hexadecyl trimethyl ammonium cations which are intercalated between the layers of the phyllosilicate and an additional modifying agent selected from the group consisting acetylcholine and choline are also part of the invention.

Throughout the description and claims the word "comprise" and variations of the word, are not intended to exclude other technical features, additives, components, or steps. Additional objects, advantages and features of the invention will become apparent to those skilled in the art upon examination of the description or may be learned by practice of the invention. The following examples and drawings are provided by way of illustration, and they are not intended to be limiting of the present invention. Reference signs related to drawings and placed in parentheses in a claim, are solely for attempting to increase the intelligibility of the claim, and shall not be construed as limiting the scope of the claim. Furthermore, the present invention covers all possible combinations of particular and preferred embodiments described herein

EXAMPLES

Example 1: Preparation of montmorillonite modified with hexadecyltrimethyl ammonium cations and acetylcholine or choline

Example 1a: montmorillonite with 5.5 CEC of HDTA and 0.5 CEC of ACO

Purified sodium montmorillonite (Closiste® Na^+) was purchased from Southern Clay Products, with moisture content between 4 and 9 % CEC of sodium montmorillonite was 92.6 mequiv/100g.

Quaternary ammonium salts were supplied by Acros Organics. Choline (CO) chloride, acetylcholine (ACO) chloride, and hexadecyltrimethyl ammonium (HDTA) bromide with 99 % of purity, and trimethyloctadecylammonium bromide 98% was purchased from Fluka.

For the production of the modified phyllosilicate modified with acetylcholine and hexadecyltrimethyl ammonium cations, 20 grams of purified sodium montmorillonite were dispersed in water at 70ºC under energetic stirring. After, 200 ml of ethanol were added. Later, the mixture was undergone an ultrasound treatment.

Then 1.48 grams of acetylcholine chloride were dissolved in 250 ml of ethanol at 70ºC. After that, phyllosilicate suspension was added slowly. Once this step was finalized, 37.12 grams of the modifier hexadecyltrimethyl ammonium bromide were dissolved in 250 ml of ethanol, and the solution previously prepared was added. After that, the solution was kept during at least 12 hours (at 70ºC) in a continuous stirring. A cation exchange reaction between the hydrated cations (inside the montmorillonite layers) and the alkyl ammonium ions was carried out in this aqueous-ethanolic solution.

The next step consists of purifying the modified phyllosilicate prepared. With this purpose 1l solution 50:50 vol water:ethanol was prepared. After filtering the mixture under vacuum, fresh solution was added to the modified phyllosilicate, and mixture was maintained under stirring at 70ºC at least 2 hours. The procedure was repeated until solution filtered was below 5 µS/cm in conductivity.

Next step includes drying of the phyllosilicate at 70ºC during at least 12 hours. Finally, phyllosilicate were milled, and sieved to a particle size below 25 microns. The modified phyllosilicate obtained is a Cloisite (CLO) with 5.5 CEC of HDTA and 0.5 CEC of ACO.

Example 1b: montmorillonite with 5.75 CEC of HDTA and 0.25 CEC of ACO

A CLO with 5.75 CEC of HDTA and 0.25 CEC of ACO was obtained following the process of Example 1b but using the ACO halide dissolved in 250 ml of ethanol. ACO mass was 0.84 grams, and HDTA mass was 38.81 grams.

Example 1c: montmorillonite with 5.75 CEC of HDTA and 0.25 CEC of CO

A CLO with 5.75 CEC of HDTA and 0.25 CEC of CO was obtained following the process of Example 1b but using 0.65 grams of CO halide dissolved in 250 ml of ethanol

Example 2. Preparation of montmorillonite modified with hexadecyltrimethyl ammonium cations

For the production of the montmorillonite modified with hexadecyltrimethyl ammonium cations, the same process of Example 1 was carried out but starting from 40.50 grams of hexadecyltrimethyl ammonium bromide which have been dissolved in 500 ml of ethanol. The modified phyllosilicate obtained is a CLO with 6 CEC of HDTA.

Comparative Example 1: Preparation of montmorillonite modified with trimethyloctadecyl ammonium (ODTA) cations

For the production of the montmorillonite modified with (ODTA) cations the same process of Example 2 was carried out but starting from 43.62 grams of (ODTA) bromide. The modified phyllosilicate obtained is a CLO with 6 CEC of ODTA.

Comparative Example 2: Preparation of Montmorillonite modified with ACO

For the production of the montmorillonite modified with (ACO) cations the same process of Example 2 was carried out but starting from 10.09 grams of (ACO) chloride. The modified phyllosilicate obtained is a CLO with 3 CEC of ACO.

Comparative Example 3: Preparation of Montmorillonite modified with CO

For the production of the montmorillonite modified with (CO) cations the same process of Example 2 was carried out but starting from 7.76 grams of (CO) chloride. The modified phyllosilicate obtained is a CLO with 3 CEC of CO.

Example 3: Thermal characterization of phyllosilicates with mixture of modifiers.

Presence of modifiers in the phyllosilicates obtained in Examples 1a, 1b and 2 was verified with thermal characterization by TGA see FIG. 1 and its stability was compared with phyllosilicates obtained in the Comparative Examples 1, 2, and 3.

Phyllosilicates prepared with a mixture of modifiers present different weight changes, which are the contribution of both modifiers. For comparison purpose, it was included in this Figure modified phyllosilicates with only one modifier (hexadecyltrimethylammonium, acetylcholine or choline). It was observed that the modified phyllosilicate, montmorillonite with octadecyltrimethylammonium was the less thermally stable, with big difference with the other modified phyllosilicates.

As most of the content of the modified phyllosilicates with a mixture of modifiers (hexadecyltrimethylammonium and acetylcholine) was hexadecyltrimethylammonium bromide, one could think that these phyllosilicates would have the same behaviour as hexadecyltrimethylammonium bromide. However, an unexpected effect was produced, and the modified phyllosilicate with a mixture of modifiers resulted to be more thermally stable in the range of temperatures between 285 and 388 ºC.

Example 4. Preparation of PLA-phyllosilicate nanocomposites

Example 4a: PLA4042-phyllosilicate (montmorillonite with 5.5 CEC of HDTA and 0.5 CEC of ACO)

PLA nanocomposites samples were obtained with the modified phyllosilicate prepared in Example 1a, and PLA 4042.

For this purpose a DSM Xplore Microcompounder (15 cc) was used. PLA pellets (dried overnight at 60ºC) were blended with 4% in weight of modified phyllosilicate in this co-rotating twin screw micro-extruder. The temperature of processing was 200ºC.The rotation speed of the screw was maintained at 100 r.p.m., and residence time was set to 10 min. After extrusion, the melted materials were transferred through a preheated cylinder, 200ºC the mini injection moulding machine (4cc) (DSM Xplore) to obtain bone-like specimen samples (ISO 527 standard; probe type 5A-B)

Example 4b: PLA4042-phyllosilicate (montmorillonite with 5.75 CEC of HDTA and 0.25 CEC of ACO)

The same process of Example 4a was carried out but with the modified phyllosilicate prepared in Example 1b.

Example 4c: PLA4042-phyllosilicate (montmorillonite with 5.75 CEC of HDTA and 0.25 CEC of CO)

The same process of Example 4a was carried out but with the modified phyllosilicate prepared in Example 1c.

Example 4d: PLA4042-phyllosilicate (montmorillonite with HDTA)

The same process of Example 4a was carried out but with the modified phyllosilicate prepared in Example 2.

Example 4e: PLA2002-phyllosilicate (montmorillonite with 5.75 CEC of HDTA and 0.25 CEC of ACO)

The same process of Example 4a was carried out but with PLA2002 and the modified phyllosilicate prepared in Example 1b.

Example 4f: PLA2002-phyllosilicate (montmorillonite with HDTA)

The same process of Example 4a was carried out but with PLA2002 and the modified phyllosilicate prepared in Example 2.

Comparative Example 4: Preparation of PLA4042-phyllosilicate (montmorillonite with ODTA)

The same process of Example 4a was carried out but with the modified phyllosilicates prepared in Comparative example 1.

Comparative Example 5: Preparation of PLA2002-phyllosilicate (montmorillonite with ODTA)

The same process of Example 4a was carried out but with PLA2002 and with the modified phyllosilicates prepared in Comparative example 1.

Example 5: Characterization of the PLA-phyllosilicate nanocomposites of Example 4.

Mechanical Properties

Mechanical properties were evaluated using a universal testing machine (model M350-20CT), following standard ISO-527.

Results were presented in FIG. 2 show the Young Modulus and the elongation at break of PLA, (nanocomposites obtained in Example 4a, 4b, and 4c).

As it can be observed in FIG. 2, young Modulus was increased in the case of PLA nanocomposite versus PLA pure, and also an increase in the elongation at break was observed (best result obtained with nanocomposites prepared in Example 4b) with respect to PLA pure. This was an unexpected result since an increase in Young Modulus generally implies a decrease in the elongation at break.

Comparative results of nanocomposites based on PLA 4042 are shown in FIG. 3. It can be seen that the use of modified phyllosilicate of the present invention produces an increase in Young Modulus, and also an increase in the elongation at break, as occurred previously in respect of the nanocomposite of comparative example 4. Elongation at break reaches higher values when nanocomposites prepared in Example 4f and 4b were used.

Water Vapour Transmission Rate (WVTR)

Samples were evaluated following the standard ASTM E96 at 23ºC and 50 % RH (Relative Humidity) (desiccant method).

Results are shown in Table 1. The smaller the value of the water vapour permeability is, the more excellent the barrier property is.

The maximum reduction in WVTR at these conditions was reached with sample wherein the modifying agent is HDTA.

Table 1. Water Vapour permeability of injected samples based on PLA 4042.

Sample	WVTR (g.mm/m^2.day)
PLA4042	5.08
Nanocomposite prepared in Example 4d	1.33
Nanocomposite prepared in Example 4b	2.31
Nanocomposite prepared in Comparative Example 4	3.17

It was observed that WVTR was reduced when the phyllosilicates are added. The nanocomposites of the inventions show a higher reduction of WVTR than the closest prior art phyllosilicates .Best results were reached with the nanocomposite prepared in Example 4d, with an improvement of 74 %.

The same samples were prepared with PLA 2002 grade; results were presented in Table 2.

Table 2. WVTR results at 23ºC and 50 % RH for the composites prepared with PLA2002.

Sample	WVTR (g.mm/m^2.day)
PLA2002	5.56
Nanocomposite prepared in Example 4f	1.85
Nanocomposite prepared in Example 4e	3.48
Nanocomposite prepared in Comparative Example 5	5.24

The nanocomposites of the inventions show a high reduction of WVTR when the phyllosilicates is added. This reduction is higher than the PLA pure and the one showed by the closest prior art phyllosilicate (comparative example 5). Best results were reached with the nanocomposite prepared in Example 4f, with an improvement of 67 %.

Oxygen transmission rate evaluation over samples prepared with PLA thermoforming grade (PLA2002D).

Oxygen transmission rate was evaluated following standard ASTM D3985: "Standard Test Method for Oxygen Gas Transmission Rate Through Plastic Film and Sheeting Using a Coulometric Sensor". Experimental equipment was an OX-TRAN 2/20 SM. The measurements conditions were 23 ºC and 50% relative humidity. The test was performed with oxygen (100 %).

Results are presented in Table 3.

The results show the reduction in oxygen permeability of the nanocomposites of the invention. The best improvement is observed with the nanocomposite prepared in Example 4b, with a reduction in oxygen permeability of almost 15%.

Table 3. Oxygen permeability results at 23 ºC and 50 % RH over the samples prepared with PLA4042 grade.

SAMPLE	Transmission rate ml / [m² - day]	Permeability ml*mm/m^2*day*Mpa	Improvement respect to neat PLA %
PLA4042	11,6	176,8	-
Nanocomposite prepared in Example 4b	9,7	150,4	14,9
Nanocomposite prepared in Example 4f	10,9	167,4	5,3
Nanocomposite prepared in Comparative Example 4	11,36	176,9	-0,1

Thermal properties

It was used a differential scanning calorimetric technique to show what happens to the different nanocomposites (Ex. 4a, 4b, 4d and Comparative Ex. 4) and PLA 4042 when reach the nanocomposites and polymer melting temperature.

The different samples were heated at a controlled rate and a plot of heat flow versus temperature was produced (FIG. 4).

For comparison purpose, it was included in this Figure neat PLA 4042. It was observed that the nanocomposites of the invention had melting point higher than PLA. The nanocomposites of the invention present similar (Ex. 4d) or better (Ex. 4a) thermal properties than the nanocomposite with octadecyltrimethylammonium.

CLAIMS

1. A modified phyllosilicate composition comprising a modifying agent which is hexadecyl trimethyl ammonium ions which are intercalated between the layers of the phyllosilicate and an additional modifying agent selected from the group consisting acetylcholine and choline.

2. A process for the preparation of the modified phyllosilicate according to claim 1, which comprises:
(a) dispersing the phyllosillicate in water and an C_1-C_{10} alcohol; (b) applying ultrasonic wave; (c) adding choline salt or acetylcholine salt; (d) adding hexadecyl trimethyl ammonium salt; (e) maintaining the mixture of step (d) at a temperature comprised between 20ºC and 120ºC; (f) isolating the compound obtained in step (d), wherein the step a), b), c) and d) can be carried out in any order.

3. The process according to claim 2, wherein the phyllosilicate is dispersed in water and ethanol.

4. The process according to any of the claims 2-3, wherein the choline salt or acetylcholine salt added is choline halide or acetylcholine halide.

5. The process according to claim 4, wherein the choline halide or acetylcholine halide added is choline chloride or acetylcholine chloride.

6. The process according to any of the claims 2-5, wherein the hexadecyl trimethyl ammonium halide added is hexadecyl trimethyl ammonium bromide.

7. The process according to any of the claims 2-6, wherein the mixture of step (d) is maintained at a temperature comprised between 65ºC and 75ºC.

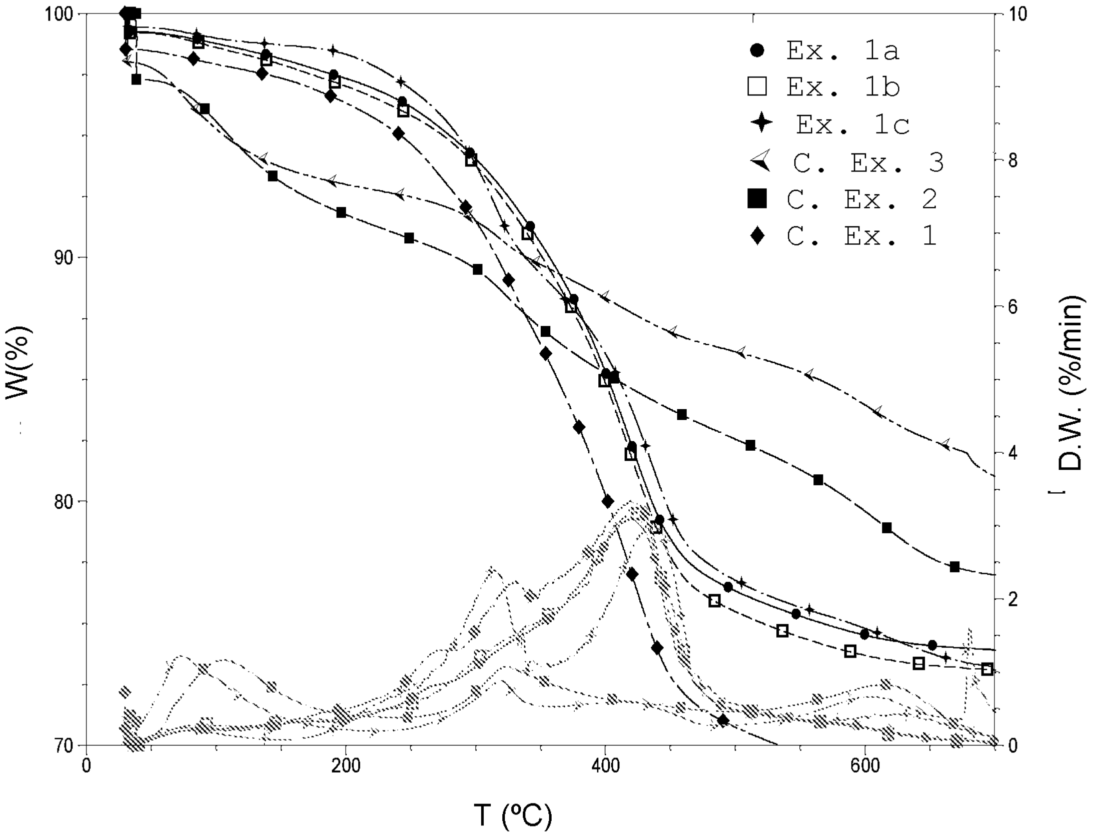
8. The process according to any of the claims 2-7, wherein the adding step first is performed with the choline or the acetylcholine and afterwards is performed with the hexadecyl trimethyl ammonium halide.

9. The process according to any of the claims 2-8, wherein the isolating step comprises purifying the modified phyllosilicate prepared.

10. The process according to claim 9, wherein the phyllosilicate is purified with a solution of water:ethanol and the mixture is maintained under stirring at a temperature comprised between 50ºC-90ºC.

11. The process according to any of the claims 2-10, wherein the isolating step comprises a drying step of the phyllosilicate after the purification, the drying step is carried out at a temperature comprised between 70ºC-90ºC.

12. Use of the modified phyllosilicate as defined in claim 1, as a reinforcing agent of polymers.


W(%)
D.W. (%/min)
T (ºC)
100
90
80
70
10
8
6
4
2
0
0
200
400
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□ Ex. 1b
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■ C. Ex. 2
♦ C. Ex. 1

FIG. 1

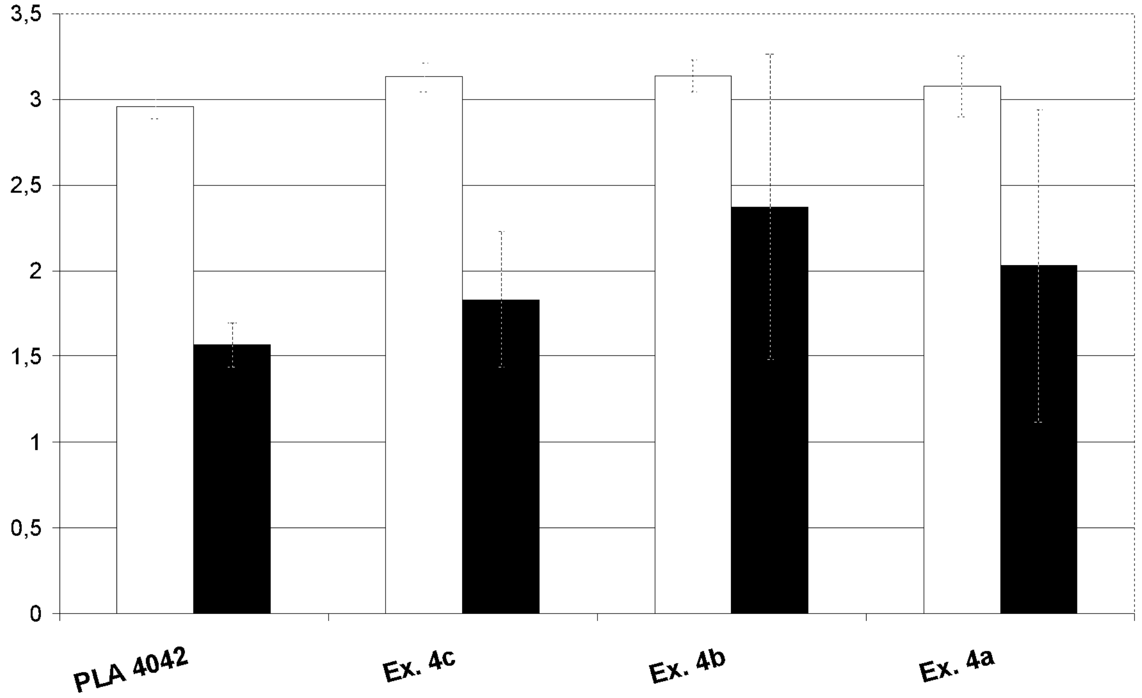

FIG. 2

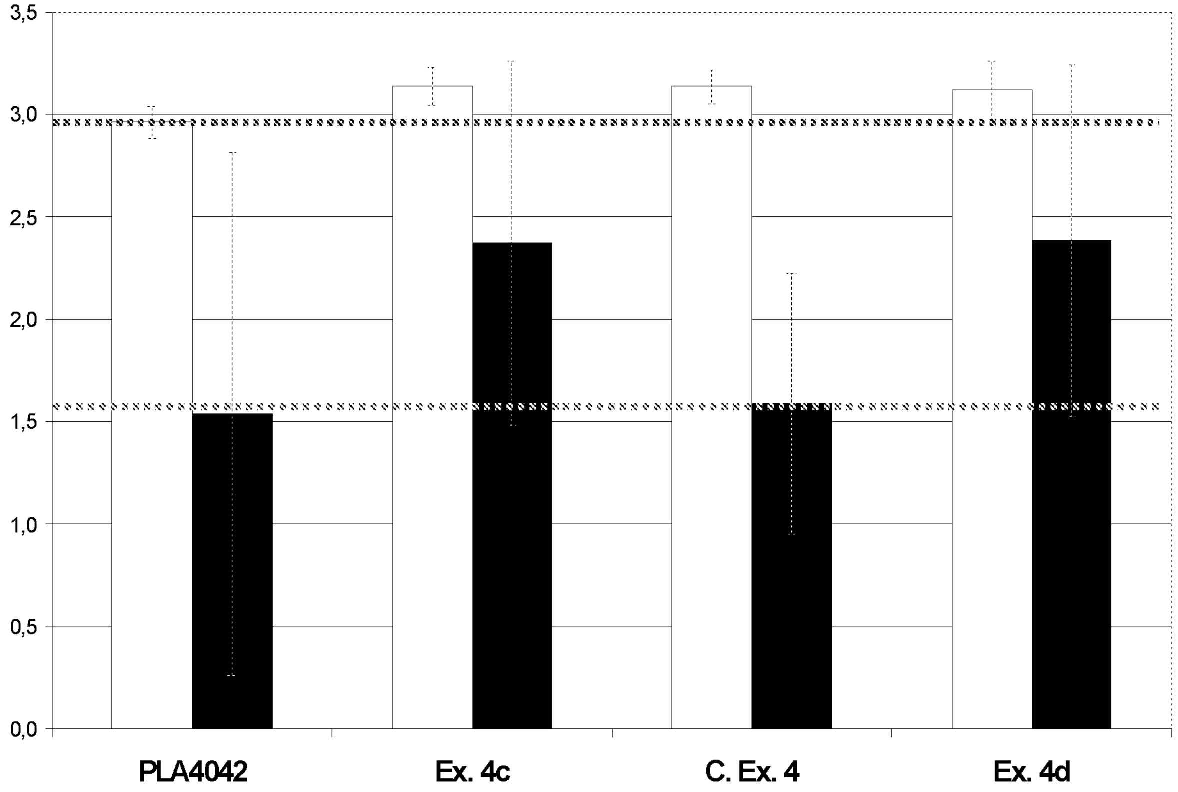

FIG. 3

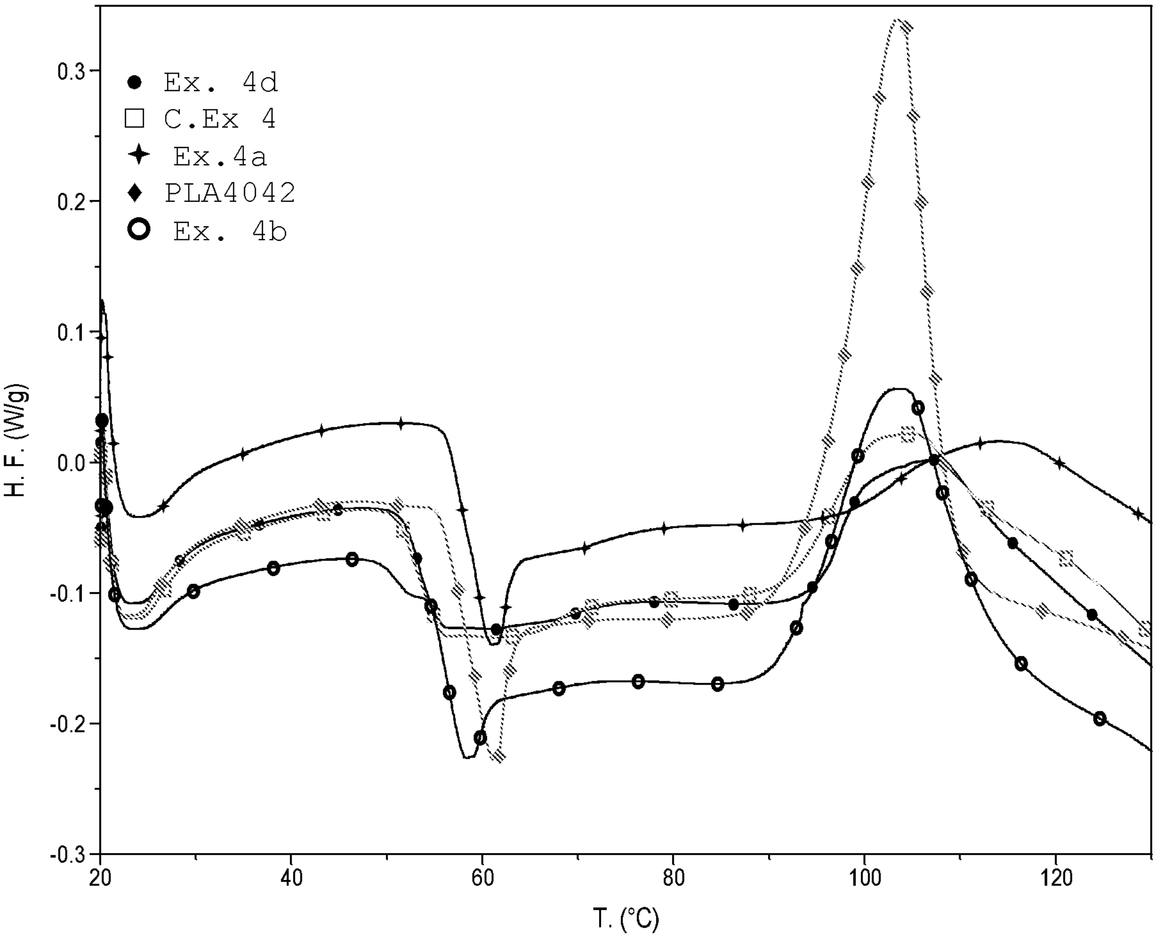
● Ex. 4d
□ C.Ex 4
✦ Ex.4a
♦ PLA4042
○ Ex. 4b
H. F. (W/g)
0.3
0.2
0.1
0.0
-0.1
-0.2
-0.3
20
40
60
80
100
120
T. (°C)

FIG. 4

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2011/063406

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08K3/34
ADD.

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C08K

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, PAJ, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	FR 2 771 308 A1 (INST FRANCAIS DU PETROLE [FR]) 28 May 1999 (1999-05-28) examples	1-12
A	EP 1 787 918 A1 (UNITIKA LTD [JP]; SHISEIDO CO LTD [JP]) 23 May 2007 (2007-05-23) claims	1-12

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

☒ See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier document but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
"&" document member of the same patent family

Date of the actual completion of the international search
1 September 2011

Date of mailing of the international search report
14/09/2011

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Devriese, Karel

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2011/063406

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
FR 2771308 A1	28-05-1999	US 6191333 B1	20-02-2001
EP 1787918 A1	23-05-2007	CN 1953911 A	25-04-2007
		HK 1100213 A1	30-04-2010
		WO 2005120978 A1	22-12-2005
		US 2008069993 A1	20-03-2008