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(71) Applicant: **USTAV MAKROMOLEKULARNI CHEMIE AV CR, V.V.I.** [CZ/CZ]; Heyrovskeho namesti 2, 16206 Praha 6 - Brevnov (CZ).

(72) Inventors: **KREDATUSOVA, Jana**; Trebickeho 741, 37701 Jindrichuv Hradec (CZ). **BENES, Hynek**; Rochovska 765, 19800 Praha 9 (CZ).

(74) Agent: **HARTVICHOVA, Katerina**; INVENTIA s.r.o., Na Belidle 3, 15000 Praha 5 (CZ).

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(54) **Title**: METHOD FOR PREPARATION OF POLYMERIC MATERIALS

(57) **Abstract**: Title of the invention: Method for preparation of polymeric materials The invention provides a method of preparation of a polymeric material, wherein at least one cyclic monomer is combined with hydrated layered double hydroxide of formula [$M^{2+}1$-xM^{3+}+x(OH)2(A^{m}-)x/m], wherein A^{m} is an m-valent anion, M^{2+} is a divalent metal cation and M^{3+} is a trivalent metal cation, the value x is in the range of $0.20 < x < 0.33$, whereas the hydrated layered double hydroxide is surface-modified by a ionic liquid containing a phosphonium cation in the amount of 0.1 to 9 wt. % relative to the weight of the hydrated layered double hydroxide, in weight ratio of the cyclic monomer to the surface-modified layered double hydroxide 100/1 to 10/1, and the resulting suspension is treated with electromagnetic irradiation with a frequency ranging from 915 to 2450 MHz at the temperature from 150 °C to 250 °C, preferably for 3 min to 120 min.

Method for preparation of polymeric materials

Field of Art

The invention relates to a method for preparation of polymeric materials filled with exfoliated layered double hydroxides.

Background Art

Polymeric materials containing layered nanofillers are popular materials for a number of applications, because they show improved barrier, mechanical and thermal properties, as well as a decreased flammability while maintaining desirable optical properties. A successful nanocomposite preparation must include delamination (disruption of the layered structure) of the filler which results in an exfoliated structure. Such exfoliated structure is the only structure combining the properties of an inorganic phase (filler) and an organic phase (polymer). Due to the nanofiller dimensions, concentration of stress and occurence of microfissures do not happen in the nanocomposites, in contrast to conventional composite materials.

Layered inorganic materials being formed by (i) negatively charged layers and exchangeable cations (Na^+, K^+, etc.) localized on the surface and between the layers (e.g. montmorillonite, saponite, hectorite, etc.), or (ii) positively charged layers containing exchangeable anions such as NO_3^-, $[CO_3]^{2-}$, etc. between the layers (e.g. hydrotalcite and its synthetic analogs, also called „layered double hydroxides“) are used as the fillers. Natural layered fillers contain only hydrated inorganic ions between the layers, and thus can only be dispergated in hydrophilic polymers. The quality of nanocomposites based on layered fillers strongly depends on the filler quality, which varies a lot in case of natural silicates. Thus, in recent years, synthetic layered materials such as layered double hydroxides have been used since their controlled synthesis guarantees homogeneity and reproducible quality of the resulting material. In order to ensure compatibility of the layered double hydroxides with a hydrophobic polymer matrix, a so-called organiphilization of the filler is performed to facilitate intercalation of polymer chains to the interlayer space (e.g. EP 2540770A2, US 7 968 740, US 7786202 B2, S. Livi et al.: Journal of Colloid and Interface Science 388 (2012) 123–129; J.U. Ha, M. Xanthos, Applied Clay Science 47 (2010) 303-310).

The preparation of an exfoliated nanocomposite is technologically rather difficult. Prior art describes methods comprising addition of a surface-modified layered filler into melted polymers (Moyo L., Makhado E., Rya SS. Journal of Applied Polymer Science 2014, 131, 41109), however, these methods are not suitable for all types of polymers, and often result only in intercalation of the filler (increased interlayer distance), but not in its complete exfoliation (Q. Wang, D. O´Hare,

Chemical Reviews, 2012, 112, 4124; M. Alexandre, P. Dubois, Materials Science and Engineering, 2000, 28, 1-63). This produces polymer materials with a non-homogeneous distribution of the filler.

Swelling of the layered filler in a suitable solvent leading to an increased interlayer distance of the filler allows intercalation of monomer, and a subsequent *in situ* polymerization of the monomer results in a nanocomposite (US 4 889 885, US 5 102 948). The limitation of this procedure consists in the need to use the solvent which must then be removed from the nanocomposite.

Fischer et al. describes a method of preparation of a nanocomposite material by *in situ* polymerization of a monomer (in particular caprolactame) in the presence of a modified layered double hydroxide (US 6 372 837; EP 1 045 876 or WO 99/35185). Modification of the filler is performed by ion-exchange reaction so that at least 20 % of the intercalated anions are formed by organic anions having the formula R'-$RCOO^-$, R'-$ROSO_3^-$ or R'-RSO_3^-, whereas R is alkyl or alkyl-phenyl group having 6-22 carbon atoms and R' is a reactive hydroxide, amine, epoxy, vinyl, carboxy, hydroxyphenyl or anhydride group. Only in one embodiment of the invention, α,ω-aminoundecanic acid is used for the ion-exchange reaction, yielding an LDH filler with a carboxy group, which – after addition of caprolactam – covalently binds to the formed polycaprolactame matrix.

Patent application WO 2006/000550 discloses a method of preparation of a nanocomposite by *in situ* polymerization of a cyclic monomer (ε-caprolactone) in the presence of an inorganic filler (hydrotalcite) without organic modification. The procedure yields an exfoliated nanocomposite, if the filler content is lower than 10 wt.%. A drawback of this procedure is a rather time demanding polymerization (4 h), as well as a low compatibility of the hydrophilic non-modified filler with the hydrophobic polymeric matrix leading to a nanocomposite with insufficient mechanical properties.

Winters et al. intercalates layered double hydroxides by organic fatty acid and natural resin anions containing 8 or more carbon atoms (US 7 968 740). Intercalation by these types of organic anions results in an increased interlayer distance (>1.5 nm), thus facilitating the delamination of the filler. In the procedure of US 2011/0003719, the organic-modified double hydroxides containing at least 10 % of organic anions are mixed with a cyclic monomer, specifically with a glycolide or a lactide, and after heating the mixture, *in situ* polymerization occurs. An example shown in the patent application only mentions polymerization of L-lactide in the presence of 2.4 wt.% of layered double hydroxide which contains C16 (43 mol. %) and C18 (43 mol. %) fatty acid anions, and 14 mol. % of hydroxide anions. The polymerization requires a long reaction time (6 h), whereas a transparent mixture indicating delamination of the filler is formed only after 1 h of heating of the suspension (Tammaro, L. et al: J Polym Sci (2005) 43, 2281)

The long reaction time is a common feature of all conventional ring-opening polymerizations. Prior art discloses procedures for microwave-accelerated cyclic monomer polymerizations for the

preparation of polylactide (RS 20070324), poly(ε-caprolactone) (CN1810848, CN 181084859, Liao L.Q. et al., Journal of Polymer Science 2002, 40, 1749-1755, Albert P. et al., Macromolecular Chemistry and Physics 1996, 197, 1633-1641, etc.), polylactide-polyglycolide, polylactide-trimethylenecarbonate or polylactide-polycaprolactone copolymers (RS 20070324), or polycaprolactone polyol (CN 102643412), using conventional catalytic and initiation systems, in particular based on metallic compounds (tin(II) 2-ethylhexanoate, tin(II) chloride, etc.), organic acids, anhydrides and compounds bearing hydroxyl groups (alcohols, phenols). JP 2014095050 describes a microwave polymerization of lactide and ε-caprolactone catalyzed by scandium compounds. Microwave polymerization of cyclic carbonate in ionic liquid media with imidazolium cation and tetrafluoroborate anion is described (CN 101880382). These works use the microwave (dielectric) heating to increase the rate of polymerization. However, they do not relate in any way to polymerization of cyclic monomers in the presence of layered double hydroxides.

The aim of the present invention is to provide a process for polymerization of cyclic monomers in the presence of layered double hydroxides which results in a polymeric material with a high conversion of the monomer, containing the filler with a completely exfoliated structure.

Disclosure of the Invention

The present invention provides a method of preparation of a polymer material filled with exfoliated layered double hydroxides, wherein at least one cyclic monomer is combined with hydrated layered double hydroxide of formula $[M^{2+}_{1-x}M^{3+}_{x}(OH)_2(A^{m-})_{x/m}]$, wherein A^{m-} is an m-valent anion, M^{2+} is a divalent metal cation and M^{3+} is a trivalent metal cation, the value x is in the range of $0.20 < x < 0.33$, whereas the hydrated layered double hydroxide is surface-modified by an ionic liquid containing a phosphonium cation in the amount of 0.1 to 9 wt. % relative to the weight of the hydrated layered double hydroxide, in weight ratio of the cyclic monomer to the surface-modified layered double hydroxide 100/1 to 10/1, and the resulting suspension is treated with electromagnetic irradiation having the frequency of 915 to 2450 MHz to the temperature from 150 °C to 250 °C, preferably for 3 min to 120 min. The polymerization proceeds without the presence of initiator and results in a polymer material with a high conversion of the monomer, containing the filler with a completely exfoliated structure.

The divalent metal cation M^{2+} may be for example a divalent cation of a metal of the group IIA of the periodic table, or a divalent cation of the first or second period of d-metals, or a mixture of said cations. Particularly preferred are divalent cations of magnesium, calcium, zinc, copper, cobalt, iron, manganese.

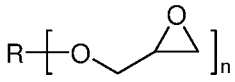
The trivalent metal cation M^{3+} may be for example a trivalent cation of a metal of the group IIIA of the periodic table, or a trivalent cation of the first or second period of d-metals, or a mixture of said cations. Particularly preferred are trivalent cations of aluminium, chromium, iron, manganese, gallium.

The anion A^{m-} may be for example carbonate, nitrate, halogenide, halogenate, sulfate, or an organic cation such as oxalate, acetate, benzoate.

The ionic liquid comprising a phosphonium cation preferably comprises a phosphonium cation of general formula $P^+R^1R^2R^3R^4$, wherein R^1, R^2, R^3, R^4 are independently selected from linear or branched C_1-C_{18} alkyls, preferably said alkyl is methyl or alkyl with even number of carbon atoms. The counterion is preferably selected from the group comprising halogenide, R^5COO^-, phosphinate, optionally comprising 1-2 R^5 chains, phosphate, optionally comprising 1-2 R^5 chains, sulfate, optionally comprising 1-2 R^5 chains, sulfonate, optionally comprising 1-2 R^5 chains, carbonate, optionally comprising 1-2 R^5 chains, benzenesulfonate, optionally comprising 1-2 R^5 chains, thiophosphinate, dithiophosphinate, dicyanoamide, tricyanoamide, bis(trifluoromethylsulfonyl)imide, tosylate, hexafluorophosphate, whereas R^5 is a linear or branched C_1-C_{14} alkyl.

In one preferred embodiment, the ionic liquid comprising a phosphonium cation may be selected from the group comprising trihexyl(tetradecyl) phosphonium bis(trifluoromethylsulfonyl) imide, tetrabutyl phosphonium chloride, ethyl(tributyl) phosphonium diethyl phosphate, tetraoctyl phosphonium bromide, tributyl(methyl) phosphonium bis(trifluoromethylsulfonyl) imide, tributyl(methyl) phosphonium methylsulfate, tetrabutyl phosphonium bromide, tributyl(tetradecyl) phosphonium chloride, tributyl(tetradecyl) phosphonium dodecylbenzen sulfonate, trihexyl(tetradecyl) phosphonium chloride, trihexyl(tetradecyl) phosphonium bis(2,4,4-trimethylpentyl) phosphinate, trihexyl(tetradecyl) phosphonium decanoate, trihexyl(tetradecyl) phosphonium bis(2-ethylhexyl) phosphate, trihexyl(tetradecyl) phosphonium dicyanoamide, trihexyl(tetradecyl) phosphonium bromide, trihexyl(tetradecyl) phosphonium tricyanomethanide, trihexyl(tetradecyl) phosphonium hexafluorophosphate, tributyl(methyl) phosphonium 1,1,2,2-tetrafluoroethane sulfonate, triisobutyl(methyl) phosphonium tosylate, tributyl(methyl) phosphonium bis(2,4,4-trimethylpentyl) thiophosphinate, tributyl(methyl) phosphonium methylcarbonate, tributyl(methyl) phosphonium bis(2,4,4-trimethylpentyl) dithiophosphinate, trioctyl(methyl) phosphonium methylcarbonate, tributyl(octyl) phosphonium chloride, and mixtures of the listed compounds.

Cyclic monomers are in particular cyclic esters, cyclic carbonates, anhydrides, lactames, epoxides, cyclic siloxanes, or mixtures thereof.

The cyclic monomer is preferably a cyclic ester containing 2-6 carbon atoms in the cycle, optionally substituted by at least one linear or branched alkyl containing 1-6 carbon atoms; a cyclic amide containing 3-12 carbon atoms in the cycle; a cyclic siloxane containing 3-6 carbon atoms in the cycle, substituted by at least one linear or branched alkyl containing 1-6 carbon atoms; a cyclic anhydride containing 4-6 carbon atoms in the cycle; a cyclic carbonate containing 3-5 carbon atoms in the cycle, optionally substituted by at least one linear or branched alkyl containing 1-6 carbon atoms; a cyclic ether containing 2-6 carbon atoms in the cycle. Furthermore, the cyclic monomer may preferably be an epoxide having the formula  , wherein n = 2-4 and the hydrocarbyl group R contains 1-50 carbon atoms and is selected from linear or branched alkyl, alkenyl, cycloalkyl, cycloalkenyl, aryl, alkylaryl, arylalkyl, whereas R can optionally be substituted by hydroxyl, amino, amido, alkoxy, keto, carboxyl, thio and thiol functional groups and may further optionally contain one or more heteroatoms selected from the group comprising oxygen, nitrogen, bromine, chlorine, fluorine, sulfur and/or one or more heteroaryl groups such as pyridyl, furyl, thienyl and/or imidazolyl.

The epoxides are preferably selected from 2,2-bis[p-(2,3-epoxypropoxy)phenyl]propane, tetrabromodiandiglycidylether, N,N,N',N'-tetraglycidyl-4,4'-diaminodiphenylmethane, diglycidylester of hexahydroftalic acid.

Mixtures of the listed cyclic monomers in any ratios can be used.

The present invention thus provides a method of preparation of polymer material filled with exfoliated layered double hydroxides. This method includes *in situ* microwave polymerization of cyclic monomers in the presence of layered double hydroxides surface-modified by ionic liquids allowing a high absorption of the microwave irradiation for (i) initiation of the cyclic monomer polymerization without the need for addition of further initiators/catalysts, and for (ii) fast delamination of the filler, leading to the formation of a homogeneous polymeric material with a completely exfoliated layers of double hydroxide. In the prepared polymer material, the ionic liquid further acts as compatibilizer improving interphase adhesion of the filler and the polymer matrix.

The experiments have suprisingly shown that when a mixture of the cyclic monomer and hydrated layered double hydroxides ($[M^{2+}_{1-x}M^{3+}_{x}(OH)_2(A^{m-})_{x/m}.]$, wherein A^{m-} is an inorganic anion, M^{2+} is a divalent metal cation and M^{3+} is a trivalent metal cation) surface-modified by ionic liquid containing phosphonium cation is heated by the action of microwave irradiation, complete

exfoliation of the filler occurs within a few minutes, and the reaction mixture becomes completely transparent. Furthermore, it was suprisingly found that further heating in the microwave reactor leads to a further viscosity increase of the reaction mixture and to polymerization of the cyclic monomer without the need to add any other polymerization initiator or catalyst. The ionic liquid bound by ionic interactions to layered double hydroxides thus has – apart from the surfactant function improving the compatibility of the filler with the polymeric matrix – also the function of an exfoliation agent and additionally initiates the ring-opening polymerization.

In the disclosure of the invention, the term „intercalation" is defined as increase of the interlayer distance of the original filler – the layered double hydroxide. The term „exfoliation" is defined herein as a complete delamination of the filler into individual layers. Level of intercalation is determined by X-ray diffraction (XRD), because the increase in the interlayer distance caused by intercalation causes a shift in basal reflexions in the diffractogram towards lower 2theta angles. A complete exfoliation is detected in the XRD spectrum as disappeaprance of the reflexions of the starting layered filler. Furthermore, the occurence of the transparent polymeric melt indicates exfoliation of the filler.

The polymerization proceeds without the presence of initiator and results in a polymeric material with a high conversion of the monomer, containing the filler with a completely exfoliated structure.

Surface modification of the layered double hydroxide is performed using ionic liquid solution so that the resulting modified layered hydroxide contains only surface-bound ionic liquid in the amount of 0.1 to 9 wt. %. The interlayer distance of the layered double hydroxide after the modification is the same as before the modification; intercalation of the ionic liquid into the layered double hydroxide thus does not proceed.

Brief Description of Drawings

Fig. 1: XRD spectra of non-modified LDH and of ionic liquid organic-modified LDH.

Fig. 2: XRD spectra of nanocomposites PCLO/LDH prepared according to examples a) 1, b) 5, c) 7 and d) 9.

Examples of Carrying Out the Invention

Materials used in the following examples:

- trihexyl(tetradecyl)phosphonium bis(2,4,4-trimethylpentyl)phosphinate – IL 104, supplier IoLiTec Inc.
- trihexyl(tetradecyl)phosphonium 2-ethyl hexanoate – IL 351, supplier IoLiTec Inc.

- trihexyl(tetradecyl)phosphonium bis (2-ethylhexyl)phosphate – IL 349, supplier IoLiTec Inc.

- ε-caprolactone (CLO) – dried over calcium hydrode and subsequently distilled at low pressure, stored in a flask closed by a three-way tap, under nitrogen atmosphere (supplier Sigma-Aldrich).

- layered double hydroxide (LDH) – PURAL MG61HT (aluminium magnesium hydroxy carbonate), interlayer distance d_{003} determined by XRD is 0.76 nm, supplier Sasol.

- lactide – purified by double crystallization from ethyl acetate, stored under nitrogen atmosphere at 4 °C, supplier Sigma-Aldrich.

- ε-caprolactame (CLA) – stored over phosphoric oxide, supplier DSM.

- 2,2'-[(1-methylethylidene)bis(4,1-phenyleneoxymethylene)]bisoxirane (DGEBA) – D.E.R.™ 332 (The Dow Chemical Company).

- Organically modified LDH-104: LDH was dispergated in 200 ml of water/THF mixture (150 ml/50 ml). 21.5 g of ionic liquid IL 104 was added to the dispersion, this corresponds to twice the anion-exchange capacity (= 3.35 meq/g). The resulting suspension was vigorously stirred at 60 °C for 24 h. The resulting precipitate was filtered and washed with water/THF mixture. The product LDH-104 was dried at 80 °C and 20 Pa for 12 h. The interlayer distance of the product determined by X-ray diffraction was 0.76 nm, this corresponds to 11.7° 2Θ (Fig. 1) and the phosphorus content determined by X-ray fluorescent method was 0.75 wt. %, corresponding to 6.8 wt. % of the ionic liquid adsorbed on the LDH surface.

- Organically modified LDH-351: LDH was dispergated in 200 ml of water/THF mixture (150 ml/50 ml). 21.5 g of ionic liquid IL 351 was added to the dispersion, this corresponds to twice the anion-exchange capacity (= 3.35 meq/g). The resulting suspension was vigorously stirred at 60 °C for 24 h. The resulting precipitate was filtered and washed with water/THF mixture. The product LDH-351 was dried at 80 °C and 20 Pa for 12 h. The interlayer distance of the product determined by X-ray diffraction was 0.76 nm, this corresponds to 11. 7° 2Θ (Fig. 1) and the carbon content determined by elemental analysis was 6 wt. %, corresponding to 9 wt. % of the ionic liquid adsorbed on the LDH surface.

- Organically modified LDH-349: LDH was dispergated in 200 ml of water/THF mixture (150 ml/50 ml). 22 g of ionic liquid IL 349 was added to the dispersion, this corresponds to twice the anion-exchange capacity (= 3.35 meq/g). The resulting suspension was vigorously stirred at 60 °C for 24 h. The resulting precipitate was filtered and washed with water/THF mixture. The product LDH-349 was dried at 80 °C and 20 Pa for 12 h. The interlayer distance of the product determined by X-ray diffraction was 0.76 nm, this corresponds to 11.7° 2Θ (Fig. 1) and the phosphorus content determined by X-ray fluorescent method was 1.1 wt. %, corresponding to 8.8 wt. % of the ionic liquid adsorbed on the LDH surface.

Example 1:

0.04 g of LDH-351 filler and 2 g of ε-caprolactone (CLO) were dosed under nitrogen atmosphere into a glass ampoule with a magnetic stirrer. The filler was dispergated in CLO for 24 hours at stirring. The reaction mixture was then heated by microwave (MW) irradiation in a monomode MW reactor with focussed field Monowave 300 (Anton Paar, Austria, f=2.45 GHz) at a constant power of 30 W. The temperature was measured by infra-red pyrometer. After 3 minutes of heating, the temperature of the polymerization mixture reached 160 °C. The product was then left to cool to room temperature. The characteristics of the obtained product are shown in Table 1. The XRD spectrum is shown in Fig. 1a.

The polymer content was determined by extraction using distilled water. The polymer was powderized, and transferred to dried and weighted S3 sintered glass. Then it was weighted (m_0), quantitatively transferred to beakers and extracted by 100 ml of water (3 times for20 minutes). The extracted material was quantitatively transferred to the sintered glass and dried at room temperature and low pressure (20 Pa) into constant weight (m_{extr}). The polymer content (y_w) was calculated as follows:

$$y_w = \frac{m_{extr}}{m_0} \cdot 100 \qquad (\%)$$

The interlayer distance (d_{003}) of LDH was determined by X-ray diffraction. The measurements were performed with powdered samples, using the diffractometer D2 PHASER with LYNXEYE detector (Bruker, Germany), Cu Kα radiation source 30 kV, 10 mA. Qualitative analysis was performed using DiffracPlus Eva (Bruker AXS, Germany) software, using the JCPDS PDF-2 database.

Transmission electron microscopy was measured on ultra thin sections prepared by ultramicrotome with cryoextension Leica Ultracut UCT, sample temperature was −80 °C. The prepared samples were transferred to a copper grid and observed by transmission electron microscope JEM 200CX (JEOL, Japan) at 100 kV. The photos were digitalized by Nikon DXM1200 camera.

Thermal properties of the prepared samples were assessed by DSC Q2000 (TA Instruments, USA). The samples were measured in the heating-cooling-heating cycle, in the temperature range of 0 – 90 °C with the rate of 10 °C/min.

The inorganic phase content was determined by thermogravimetric analysis as incombustible residue at 500 °C in oxygen atmosphere. Analysator TGA Pyris 1 (Perkin Elmer, USA) was used for the measurement.

Example 2:

0.04 g of LDH-351 filler and 2 g of ε-caprolactone were dosed under inert nitrogen atmosphere into a glass ampoule with a magnetic stirrer. The filler was dispergated in CLO for 24 hours at stirring. The reaction mixture was then heated by MW irradiation in a monomode MW reactor with focussed field Monowave 300 (Anton Paar, Austria, f=2.45 GHz) at a constant power of 30 W. The temperature was measured by infra-red pyrometer. The temperature of the polymerization mixture continuously increased during the polymerization and after 15 minutes of heating reached 197 °C. After 15 minutes of heating, the product was left to cool to room temperature. The methods of determination of properties of the prepared polymeric nanocomposites are described in Example 1, and the results are shown in Table 1.

Example 3:

0.04 g of LDH-351 filler and 2 g of ε-caprolactone were dosed under inert nitrogen atmosphere into a glass ampoule with a magnetic stirrer. The filler was dispergated in CLO for 24 hours at stirring. The reaction mixture was then heated by MW irradiation in a monomodal focussed field MW reactor Monowave 300 (Anton Paar, Austria, f=2.45 GHz) at a constant temperature of 180 °C. The temperature was measured by infra-red pyrometer. After 20 minutes of heating, the product was left to cool to room temperature. The properties of prepared polymeric nanocomposites were determined using the methods described in Example 1, and the results are shown in Table 1.

Example 4:

0.12 g of LDH-351 filler and 2 g of ε-caprolactone were dosed under inert nitrogen atmosphere into a glass ampoule with a magnetic stirrer. The filler was dispergated in CLO for 24 hours at stirring. The reaction mixture was then heated by MW irradiation in a monomode MW reactor with focussed field Monowave 300 (Anton Paar, Austria, f=2.45 GHz) at a constant power of 30 W. The temperature was measured by infra-red pyrometer. After 3 minutes of heating, the temperature of the polymerization mixture reached 146 °C. The product was then left to cool to room temperature. The properties of prepared polymeric nanocomposites were determined using the methods described in Example 1, and the results are shown in Table 1.

Example 5:

0.04 g of LDH-104 filler and 2 g of ε-caprolactone were dosed under inert nitrogen atmosphere into a glass ampoule with a magnetic stirrer. The filler was dispergated in CLO for 24 hours at stirring. The reaction mixture was then heated by MW irradiation in a monomode MW reactor with focussed field Monowave 300 (Anton Paar, Austria, f=2.45 GHz) at a constant power of 30 W.

The temperature was measured by infra-red pyrometer. After 3 minutes of heating, the temperature of the polymerization mixture reached 162 °C. The product was then left to cool to room temperature. The properties of prepared polymeric nanocomposites were determined using the methods described in Example 1, and the results are shown in Table 1. The XRD spectrum is shown in Fig. 1b.

Example 6:

0.12 g of LDH-104 filler and 2 g of ε-caprolactone were dosed under inert nitrogen atmosphere into a glass ampoule with a magnetic stirrer. The filler was dispergated in CLO for 24 hours at stirring. The reaction mixture was then heated by MW irradiation in a monomode MW reactor with focussed field Monowave 300 (Anton Paar, Austria, f=2.45 GHz) at a constant power of 30 W. The temperature was measured by infra-red pyrometer. After 3 minutes of heating, the temperature of the polymerization mixture reached 160 °C. The product was then left to cool to room temperature. The properties of prepared polymeric nanocomposites were determined using the methods described in Example 1, and the results are shown in Table 1.

Example 7:

0.04 g of LDH-349 filler and 2 g of ε-caprolactone were dosed under inert nitrogen atmosphere into a glass ampoule with a magnetic stirrer. The filler was dispergated in CLO for 24 hours at stirring. The reaction mixture was then heated by MW irradiation in a monomode MW reactor with focussed field Monowave 300 (Anton Paar, Austria, f=2.45 GHz) at a constant power of 30 W. The temperature was measured by infra-red pyrometer. After 3 minutes of heating, the temperature of the polymerization mixture reached 154 °C. The product was then left to cool to room temperature. The properties of prepared polymeric nanocomposites were determined using the methods described in Example 1, and the results are shown in Table 1. XRD spectrum is shown in Fig. 1c.

Example 8:

0.12 g of LDH-349 filler and 2 g of ε-caprolactone were dosed under inert nitrogen atmosphere into a glass ampoule with a magnetic stirrer. The filler was dispergated in CLO for 24 hours at stirring. The reaction mixture was then heated by MW irradiation in a monomode MW reactor with focussed field Monowave 300 (Anton Paar, Austria, f=2.45 GHz) at a constant power of 30 W. The temperature was measured by infra-red pyrometer. After 3 minutes of heating, the temperature of the polymerization mixture reached 151 °C. The product was then left to cool to room temperature. The properties of prepared polymeric nanocomposites were determined using the methods described in Example 1, and the results are shown in Table 1.

Example 9:

0.75 g of LDH-104 filler and 50 g of CLO were dosed under inert atmosphere into a three-neck glass flask with an anchor stirrer. The filler was dispergated in CLO for 24 hours at stirring. The reaction mixture was then heated by MW irradiation in a multimode MW reactor (Romill, Czech Republic, f=2.45 GHz) at a constant power of 200 W. The temperature was measured by infra-red pyrometer. After 9 minutes of heating, the temperature of the polymerization mixture reached 193 °C. The product was then left to cool to room temperature. The properties of prepared polymeric nanocomposites were determined using the methods described in Example 1, and the results are shown in Table 1. XRD spectrum is shown on Fig. 1d.

Example 10:

0.6 g of LDH-104 filler and 30 g of D,L-lactide were dosed under inert atmosphere into a three-neck glass flask with an anchor stirrer. D,L-lactide was melted in oil bath and the filler was dispergated in the D,L-lactide for 20 minutes at stirring. The reaction mixture was then heated by MW irradiation in a multimode MW reactor (Romill, Czech Republic, f=2.45 GHz) at a constant power of 200 W. The temperature was measured by infra-red pyrometer. After 10 minutes of heating, the temperature of the polymerization mixture reached 185 °C. The product was then left to cool to room temperature. Completely transparent material showing only one value of glass transition temperature (40 °C) and having the polymer content of 94 %. The properties of prepared polymeric nanocomposites were determined using the methods described in Example 1, and the results are shown in Table 1.

Example 11:

0.75 g of LDH-104 filler, 30 g of CLO and 20 g of ε-caprolactame (CLA) were dosed under inert atmosphere into a three-neck glass flask with an anchor stirrer as follows: CLA was melted in oil bath and the filler was dispergated in CLA for 30 minutes at stirring. CLO was then added to the mixture and the reaction mixture was heated by MW irradiation in a multimode MW reactor (Romill, Czech Republic, f=2.45 GHz) at a constant power of 200 W. The temperature was measured by infra-red pyrometer. After 15 minutes of heating, the temperature of the polymerization mixture reached 163 °C. The product was then left to cool to room temperature. The material showing the value of glass transition temperature -10 °C and melting temperature of 102 °C. Polymer content of 86 % was determined by extraction method. The properties of prepared polymeric nanocomposites were determined using the methods described in Example 1, and the results are shown in Table 1.

Example 12:

0.12 g of LDH-104 filler and 2 g of epoxy resin DGEBA were dosed under inert nitrogen atmosphere into a glass ampoule with a magnetic stirrer. The filler was dispergated in DGEBA for 1 hour at 60 °C and stirring. The reaction mixture was then heated by MW irradiation in a monomode MW reactor with focussed field Monowave 300 (Anton Paar, Austria, f=2.45 GHz) at a constant power of 50 W. The temperature was measured by infra-red pyrometer. After 20 minutes of heating, the temperature of the polymerization mixture reached 150 °C. The product was then left to cool to room temperature. Degree of conversion of epoxy groups and glass transition temperature of the obtained product were determined by DSC, and the content of inorganic phase was determined by TGA (see Example 1). The results are shown in Table 1.

Comparative example 1:

0.1 g of LDH-104 filler and 5 g of ε-caprolactone were dosed under inert nitrogen atmosphere into a glass ampoule with a magnetic stirrer. The filler was dispergated in CLO for 24 hours at stirring. Then, under inert atmosphere, 0.18 g tin 2-ethylhexanoate was added to the reaction mixture, as initiator of CLO polymerization. The reaction mixture was then heated in oil bath for 4 h at 150 °C. Afterwards, the reaction mixture was taken out of the bath and left to cool to room temperature. The polymerization did not proceed to a high degree and yielded a liquid product with LDH-104 precipitated in the bottom of the reaction vessel.

Comparative example 2:

2 g of ε-caprolactone was dosed under inert nitrogen atmosphere into a glass ampoule with a magnetic stirrer. CLO was heated by MW irradiation in a monomodal focussed field MW reactor Monowave 300 (Anton Paar, Austria, f=2.45 GHz) at a constant power of 30 W. The temperature was measured by infra-red pyrometer. After 4 minutes of heating, the temperature of CLO reached 240 °C. CLO did not show any signs of thermic polymerization.

Comparative example 3:

0.75 g of LDH (without organic modification) and 50 g of CLO were dosed under inert atmosphere into a 250ml three-neck glass flask with an anchor stirrer. The filler was dispergated in CLO for 24 hours at stirring. The reaction mixture was then heated by MW irradiation in a multimode MW reactor (Romill, Czech Republic, f=2.45 GHz) at a constant power of 200 W. The temperature was measured by infra-red pyrometer. After 10 minutes of heating, the temperature of the polymerization mixture reached 250 °C. The product was then left to cool to room temperature. Polymer content reached only 7 wt. %.

Comparative example 4:

0.1 g of a filler intercalated by phosphonium ionic liquid trihexyl tetradecyl phosphonium dodecylsulfonate with the interlayer distance d_{003} of 3.4 nm and 5 g of ε-caprolactone were dosed into a glass ampoule with a magnetic stirrer. The filler was dispergated in CLO for 24 hours at stirring. The reaction mixture was then heated by MW irradiation in a monomodal focussed field MW reactor Monowave 300 (Anton Paar, Austria, f=2.45 GHz) at a constant power of 30 W. The temperature was measured by infra-red pyrometer. After 5 minutes of heating, the temperature of the polymerization mixture reached 250 °C. The product was then left to cool to room temperature. The obtained product had the polymer content of 5 wt. % only.

Table 1: Product charakteristics

	Description	y_w, (wt. %)	w_R, (wt. %)	d_{003}, (nm)	T_m, (°C)
Example 1	2 % LDH-351 + CLO, MW 30 W, 3 min	97.2	1.9	> 1.7*	59
Example 2	2 % LDH-351 + CLO, MW 30 W, 15 min	97.6	1.7	> 1.7*	59
Example 3	2 % LDH-351 + CLO, MW 180°C, 20 min	98.4	1.9	> 1.7*	59
Example 4	5.7 % LDH-351 + CLO, MW 30 W, 3 min	87.9	4.9	> 1.7*	57
Example 5	2% LDH-104 + CLO, MW 30 W, 3 min	96.9	2.0	> 1.7*	60
Example 6	5.7 % LDH-104 + CLO, MW 30 W, 3 min	93.4	3.8	> 1.7*	61
Example 7	2 % LDH-349 + CLO, MW 30 W, 3 min	96.9	1.7	> 1.7*	59
Example 8	5.7 % LDH-349 + CLO, MW 30 W, 3 min	84.2	3.9	> 1.7*	55
Example 9	1.5 % LDH-104 + CLO, MW 200 W, 9 min	86.2	1.7	> 1.7*	57
Example 10	2 % LDH-104 + lactide, MW 200 W, 10 min	94	2.1	> 1.7*	40**
Example 11	1.5 % LDH-104 + CLO+CLA, MW 200 W, 15 min	86	1.6	> 1.7*	102, -10**
Example 12	5.7 % LDH-104 + DGEBA, MW 50 W, 20 min	99.6***	4.5	> 1.7*	230**
Comparative example 1	2 % LDH-104 + CLO, 150°C, 4 h	14.7	-	-	-
Comparative example 2	CLO, MW 30 W, 4 min	0	-	-	-
Comparative example 3	1.5 % LDH (non-modified) + CLO, MW 200 W, 20 min	7	-	-	-
Comparative example 4	2 % intercalated LDH + CLO, MW 30 W, 10 min	5	-	-	-

$\mathbf{y_w}$ – polymer content determined by extraction in water; $\mathbf{w_R}$ – filler content determined by TGA as incombustible residue at 500°C in N_2 atmosphere; $\boldsymbol{d_{003}}$ – interlayer distance determined by X-ray diffraction; $\boldsymbol{T_m}$ – melting temperature determined by DSC; **-** value not determined; **MW 30 W** – polymerization in monomode microwave reactor at constant power 30 W; **MW 50 W** – polymerization in monomode microwave reactor at constant power 50 W; **MW 200 W** – polymerization in multimode microwave reactor at constant power 200 W

* Exfoliated structure

** Glass transition temperature determined by DSC

*** Epoxy group conversion determined by DSC

Industrial Applicability

The materials prepared by the method of the invention can be used separately for production of biodegradable packaging materials, or in mixtures with other polymers for production of filled materials.

CLAIMS

1. A method for preparation of a polymer material, **characterized in that** at least one cyclic monomer is combined with hydrated layered double hydroxide of formula $[M^{2+}_{1-x}M^{3+}_{x}(OH)_2(A^{m-})_{x/m}]$, wherein A^{m-} is an m-valent anion, M^{2+} is a divalent metal cation and M^{3+} is a trivalent metal cation, the value x is in the range of $0.20 < x < 0.33$, whereas the hydrated layered double hydroxide is surface-modified by a ionic liquid containing a phosphonium cation in the amount of 0.1 to 9 wt. % relative to the weight of the hydrated layered double hydroxide, in weight ratio of the cyclic monomer to the surface-modified layered double hydroxide from 100/1 to 10/1, and the resulting suspension is treated with electromagnetic irradiation of a frequency ranging from 915 to 2450 MHz at the temperature from 150 °C to 250 °C, preferably for 3 min to 120 min.

2. The method according to claim 1, wherein the divalent metal cation M^{2+} is a divalent cation of a metal of the group IIA of the periodic table, or a divalent cation of the first or second period of d-metals, or a mixture of said cations; preferably, M^{2+} is selected from divalent cations of magnesium, calcium, zinc, copper, cobalt, iron, manganese.

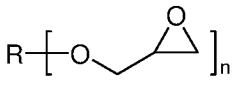
3. The method according to claim 1, wherein the trivalent metal cation M^{3+} is a trivalent cation of a metal of the group IIIA of the periodic table, or a trivalent cation of the first or second period of d-metals, or a mixture of said cations; preferably, M^{3+} is selected from trivalent cations of aluminium, chromium, iron, manganese, gallium.

4. The method according to any one of the preceding claims, wherein the anion A^{m-} is selected from the group comprising carbonate, nitrate, halogenide, halogenate, sulfate, oxalate, acetate, benzoate.

5. The method according to any one of the preceding claims, wherein the ionic liquid comprises a phosphonium cation of general formula $P^+R^1R^2R^3R^4$, wherein R^1, R^2, R^3, R^4 are independently selected from linear or branched C_1-C_{18} alkyls, preferably said alkyl is methyl or alkyl with even number of carbon atoms; whereas the counterion is selected from the group comprising halogenide, R^5COO^-, phosphinate, optionally comprising 1-2 R^5 chains, phosphate, optionally comprising 1-2 R^5 chains, sulfate, optionally comprising 1-2 R^5 chains, sulfonate, optionally comprising 1-2 R^5 chains, carbonate, optionally comprising 1-2 R^5 chains, benzenesulfonate, optionally comprising 1-2 R^5 chains, thiophosphinate, dithiophosphinate, dicyanoamide, tricyanoamide, bis(trifluoromethylsulfonyl)imide, tosylate, hexafluorophosphate, whereas R^5 is a linear or branched C_1-C_{14} alkyl.

6. The method according to any one of the preceding claims, wherein the phosphonium ionic liquid is a ionic liquid selected from the group comprising trihexyl(tetradecyl) phosphonium bis(trifluoromethylsulfonyl) imide, tetrabutyl phosphonium chloride, ethyl(tributyl) phosphonium diethyl phosphate, tetraoctyl phosphonium bromide, tributyl(methyl) phosphonium bis(trifluoromethylsulfonyl) imide, tributyl(methyl) phosphonium methylsulfate, tetrabutyl phosphonium bromide, tributyl(tetradecyl) phosphonium chloride, tributyl(tetradecyl) phosphonium dodecylbenzen sulfonate, trihexyl(tetradecyl) phosphonium chloride, trihexyl(tetradecyl) phosphonium bis(2,4,4-trimethylpentyl) phosphinate, trihexyl(tetradecyl) phosphonium decanoate, trihexyl(tetradecyl) phosphonium bis(2-ethylhexyl) phosphate, trihexyl(tetradecyl) phosphonium dicyanoamide, trihexyl(tetradecyl) phosphonium bromide, trihexyl(tetradecyl) phosphonium tricyanomethanide, trihexyl(tetradecyl) phosphonium hexafluorophosphate, tributyl(methyl) phosphonium 1,1,2,2-tetrafluoroethane sulfonate, triisobutyl(methyl) phosphonium tosylate, tributyl(methyl) phosphonium bis(2,4,4-trimethylpentyl) thiophosphinate, tributyl(methyl) phosphonium methylcarbonate, tributyl(methyl) phosphonium bis(2,4,4-trimethylpentyl) dithiophosphinate, trioctyl(methyl) phosphonium methylcarbonate, tributyl(octyl) phosphonium chloride, and mixtures thereof.

7. The method according to any one of the preceding claims, wherein the cyclic monomer is selected from the group comprising cyclic esters containing 2-6 carbon atoms in the cycle, optionally substituted by at least one linear or branched alkyl containing 1-6 carbon atoms; cyclic amides containing 3-12 carbon atoms in the cycle; cyclic siloxanes containing 3-6 carbon atoms in the cycle, substituted by at least one linear or branched alkyl containing 1-6 carbon atoms; cyclic anhydrides containing 4-6 carbon atoms in the cycle; cyclic carbonates containing 3-5 carbon atoms in the cycle, optionally substituted by at least one linear or branched alkyl containing 1-6 carbon atoms; cyclic ethers containing 2-6 carbon atoms in the cycle; epoxides having the formula



, wherein n = 2-4 and the hydrocarbyl group R contains 1-50 carbon atoms and is selected from linear or branched alkyl, alkenyl, cycloalkyl, cycloalkenyl, aryl, alkylaryl, arylalkyl, whereas R can optionally be substituted by hydroxyl, amino, amido, alkoxy, keto, carboxyl, thio and thiol functional groups and may further optionally contain one or more heteroatoms selected from the group comprising oxygen, nitrogen, bromine, chlorine, fluorine, sulfur and/or one or more heteroaryl groups such as pyridyl, furyl, thienyl and/or imidazolyl.

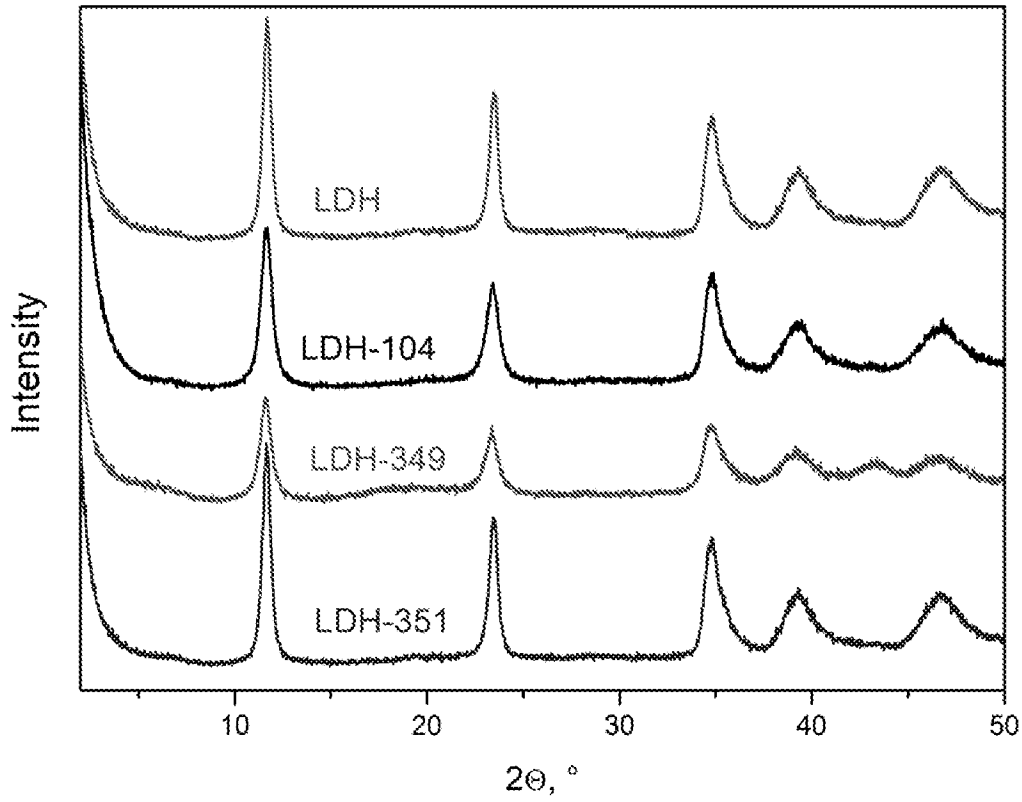

LDH
LDH-104
LDH-349
LDH-351
Intensity
10
20
30
40
50
2Θ, °

Fig. 1

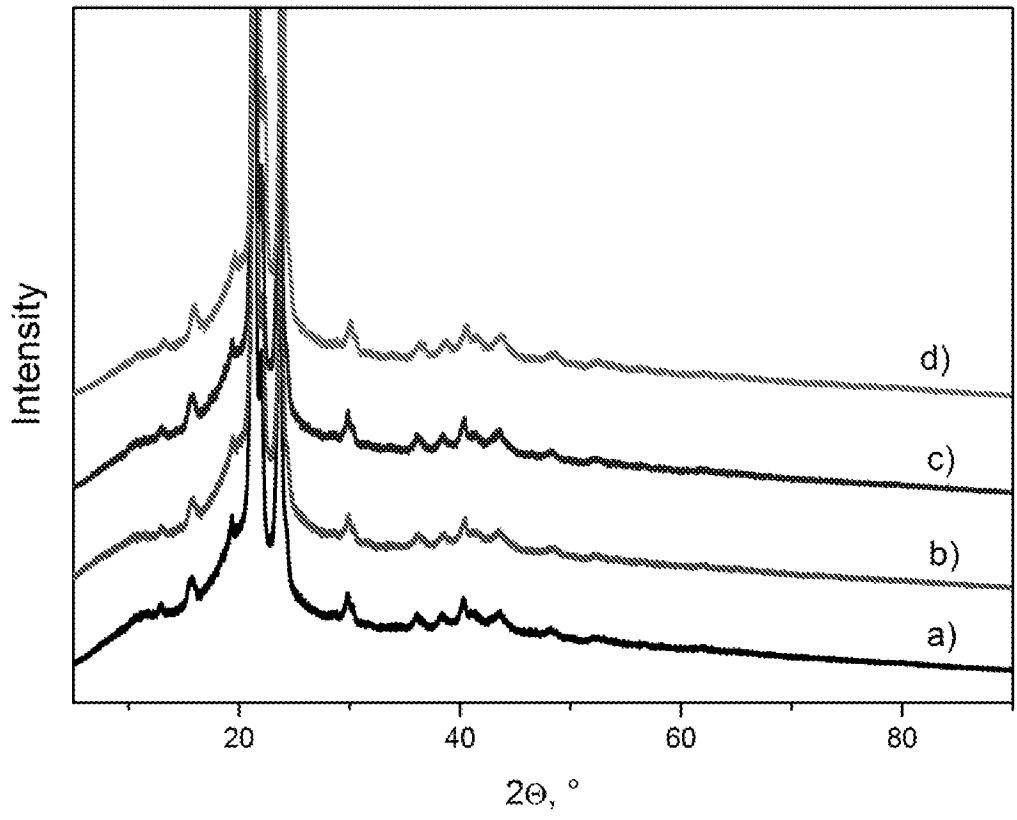

d)
c)
b)
a)
Intensity
20
40
60
80
2Θ, °

Fig. 2

INTERNATIONAL SEARCH REPORT

International application No
PCT/CZ2016/050040

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08K9/04 C08G59/22 C08G63/78 C08G69/16
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 C08G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	LIQIONG LIAO; CHAO ZHANG; SHAOQIN GONG: "Microwave-assisted synthesis and characterization of poly([epsilon]-caprolactone)/ montmorillonite nanocomposites", MACROMOLECULAR CHEMISTRY AND PHYSICS, vol. 208, no. 12, 19 June 2007 (2007-06-19), pages 1301-1309, XP002766677, cited in the application page 1302	1-7

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[X] Further documents are listed in the continuation of Box C. [ ] See patent family annex.

* Special categories of cited documents :

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

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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Date of the actual completion of the international search	Date of mailing of the international search report
2 February 2017	21/02/2017

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Masson, Patrick

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INTERNATIONAL SEARCH REPORT

International application No
PCT/CZ2016/050040

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	MARTINEZ-GALLEGOS S; HERRERO M; RIVES V: "In situ microwave-assisted polymerization of polyethylene terephtalate in layered double hydroxides", JOURNAL OF APPLIED POLYMER SCIENCE, vol. 109, no. 3, 17 April 2008 (2008-04-17), pages 1388-1394, XP002766678, page 1389	1-7
A	LIVI SÉBASTIEN ET AL: "Synthesis and physical properties of new layered double hydroxides based on ionic liquids: Application to a polylactide matrix", ANALYTICAL SCIENCES, vol. 388, no. 1, 28 August 2012 (2012-08-28), pages 123-129, XP028944820, ISSN: 0021-9797, DOI: 10.1016/J.JCIS.2012.08.031 cited in the application page 124; figure 4; table 3	1-7
A	KATIYAR V ET AL: "Poly l-lactide-layered double hydroxide nanocomposites via in situ polymerization of l-lactide", POLYMER DEGRADATION AND STABILITY, BARKING, GB, vol. 95, no. 12, 5 August 2010 (2010-08-05), pages 2563-2573, XP027527419, ISSN: 0141-3910 [retrieved on 2010-11-25] page 2564 - page 2565	1-7
A	CHAN Y N ET AL: "Preparation of clay/epoxy nanocomposites by layered-double-hydroxide initiated self-polymerization", POLYMER, ELSEVIER SCIENCE PUBLISHERS B.V, GB, vol. 49, no. 22, 17 October 2008 (2008-10-17), pages 4796-4801, XP025507720, ISSN: 0032-3861, DOI: 10.1016/J.POLYMER.2008.08.062 [retrieved on 2008-09-16] page 4797	1-7

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