Patenting Activity in Manufacturing Organoclays for Nanocomposite Applications

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Abstract

For the last two decades, intensive research has been focused on developing reinforced polymers with incorporation of nanometric fillers. Amongst the different types of nanofillers, those based on layered silicates (commonly known as clays), have been most widely investigated. Dispersing clay sheets on a nanoscopic scale (so-called exfoliation) indeed allows materials with enhanced thermal, mechanical, rheological, flame retardancy and barrier properties to be produced. However, the nanocomposite performances are strongly dependent upon the extent of clay exfoliation. In order to enhance the compatibility between the pristine clay, hydrophilic, and the polymer, hydrophobic, and to achieve a good delamination of the nanolayers, an organo-modification of the clay is most usually necessary. This mini-review will provide an outline of patenting activity in the field of manufacturing organoclays through ionic exchange. The variety of organic modifiers and the diverse processing techniques will be detailed, aiming to extract the most relevant organoclays for successful nanocomposite formation at industrial scale.

Keywords: Clay; organoclay;, nanoclay; layered silicate; ion-exchange; exfoliation.

INTRODUCTION

The layered silicates commonly used in nanocomposites belong to the structural family known as the 2:1 phyllosilicates, same as the better known minerals talc and mica. Their crystal lattice has a layered structure consisting of two dimensional layers where an octahedral sheet of aluminum or magnesium oxide is sandwiched between two external silica tetrahedral sheets. The layer thickness is around 1nm and the lateral dimensions may vary from 30nm to several microns and even larger depending on the particular silicate [1]. The regularly stacked layers are separated by a van der Waals gap, called the interlayer or the gallery. Due to the isomorphic substitution within the layers (for example Al³⁺ replaced by Mg²⁺ or by Fe²⁺, or Mg²⁺ replaced by Li⁺), negative charges are generated and are counterbalanced by mono- or divalent cations located in the interlayer Fig. (1).

These intercalated inorganic cations naturally tend to be hydrated. In presence of excess water, this natural hydration allows the stacked structure to swell. This capacity to swell by incorporating water and even organic molecules is characteristic of clay minerals such as those belonging to the smectite family and has been used for many years to develop a large number of applications [2]. Combining high swelling and cation exchange ability enables the easy replacement of the inorganic cations located in the interlayer by organic cations like tetraalkylammonium cations or protonated alkyl-amines, resulting in the formation of organically modified clays, also called organoclays.

These organoclays have found a large market providing thickening or rheological properties to an increasingly wide variety of liquids including paints, coatings, inks, adhesives and similar products [3]. Patents in this field reveal efforts to enhance the dispersibility of organoclay gellants [4] or their biodegradability [5]. Another example of application of organoclays is the purification of oil-contaminated water [6, 7]. Indeed, a surfactant adsorbed between layers of clay mineral with high swellability leads to effective adsorption of organic compounds, which can thus easily be removed from the groundwater by precipitation.

Among other research topics, the development of plastic nano-additives is however attracting the greatest deal of attention. Early work using organoclays in the preparation of nanocomposites is reflected in US Patent 2531396 [8]. This patent published in 1950 teaches the use of organically modified bentonites (phyllosilicate from the

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smectite family) to provide structural reinforcement to elastomer, such as rubber, polychloroprene and polyvinyl compounds but the results were unsatisfactory. The maximal modulus enhancement was only around 200% although the clay loading was as much as 50 wt%. The failure was obvious because clay particles existed as agglomerated tactoids. Such a poor dispersion of the silicate minerals could improve material rigidity, but certainly sacrificed the strength, the elongation at break and the toughness of the materials [9].

Over a generation later, the first major breakthrough occurred, when Kamigaito and Fukushima from Toyota Central Research and Development Co. Inc. (TCRD) demonstrated that the adsorption of a monomer between the galleries of the pristine clay with a silane coupling agent could promote the formation of an intercalated composite [10]. This invention was followed by a number of patents from TCRD between 1987 and 1990, demonstrating the use organoclay additives for plastics, for example to replace steel components in automobiles [11-16].

Fig. (1). Structure of 2:1 phyllosilicates.

Since then, development of polymer/clay nanocomposites (PCN) has been focused on improving the extent of exfoliation of the clay sheets and the enhancement of several key properties such as thermal, mechanical, rheological, flame retardancy and barrier properties of the materials. To achieve this goal, different preparation methods are used [9]. A first one is the in situ intercalation polymerization technique, in which the organoclay is swollen by the monomer (either in liquid state or in solution) so that the polymer formation can occur in between the intercalated sheets. Polymerization can be initiated either by heat or radiation, by the diffusion of a suitable initiator or by an organic initiator or catalyst fixed by ion-exchange inside the interlayer before the swelling step by the monomer.

The intercalation of polymer or pre-polymer from solution is another preparative method, based on a solvent system in which the polymer or pre-polymer is soluble and the silicate layers are swellable. After swelling the clay in an appropriate solvent, the polymer and clay solutions are mixed and subsequently, the polymer chains intercalate and displace the solvent within the interlayer of the silicate. Upon solvent removal, the intercalated structure remains, resulting in a PCN.

The third preparation process is the melt intercalation technique. This method involves annealing, statically or under shear, a mixture of the polymer and the organoclay above the softening temperature of the polymer. During annealing and if sufficient affinity exists between the polymer chains and the interlayer environment, the polymer chains diffuse from the bulk polymer melt into the gallery of the organoclay. This latter method is industrially preferred since it permits the use of conventional processing techniques such as injection molding or extrusion. Several recent reviews covering the nanocomposite research can be found in the literature [9, 17-19].
In this paper, we will focus on the manufacturing of organoclay, by reviewing for each nanocomposite preparation method the organic modifiers used and the diverse processing media for the ionic exchange process. A final note will be dedicated to the utilization of clay-concentrated blends, also referred to as masterbatches.

ORGANOCLAYS FOR IN SITU INTERCALATIVE POLYMERIZATION METHOD

In 1993, Usuki et al. successfully prepared, for the first time, exfoliated Nylon 6/clay hybrid, via in situ ring-opening polymerization of ε-caprolactam, in which alkylammonium-modified layered silicate was thoroughly dispersed in advance [20]. It was found that organophilic clay that had been ion-exchanged with 12-aminododecanoic acid could be swollen by molten ε-caprolactam. The evidence of swelling was revealed by the measurement of the interlayer distance by Small Angle X-ray Scattering (SAXS). This technique records the intensity of incident rays at very low angles (0.1 to 10°). Considering the layered silicate as a crystalline solid, the scattering angle can be related to the gallery distance. Indeed, for a crystalline solid, the incident waves are scattered from lattice planes separated by the interplaner distance \( d \) Fig. (2). Where the scattered waves interfere constructively, the path difference between two planes is given by \( 2d\sin\theta \), where \( \theta \) is the scattering angle [21]. This leads to Bragg’s law which describes the condition for constructive interference from successive crystallographic planes \((h,k,l)\) of the crystalline lattice:

\[
2d\sin\theta = n\lambda.
\]

where \( n \) is an integer determined by the order given and \( \lambda \) is the wavelength of the cathode (usually Cu).

Montmorillonite, the natural clay used by Usuki et al., has an interlayer distance of 1.1 nm. The organomodification with 12-aminododecanoic acid led to a gallery of 1.7 nm that was further expanded to 3.5 nm after swelling by ε-caprolactam [20]. Then, the monomer was polymerized in the clay gallery and the silicate layers were dispersed in Nylon 6 to yield a Nylon 6-clay hybrid (NCH) [22]. That was the first example of an industrial clay-based polymer nanocomposite Fig. (3).

For a clay loading of 2 wt\%, the modulus of the NCH increased to 1.5 times that of Nylon 6, the heat distortion temperature increased by 80°C (from 65°C for pure Nylon-6 to 140°C for the NCH) and the gas barrier effect was doubled [23]. Messersmith et al. prepared NCH in the same manner and obtained a decrease in gas permeability of about 20% under 4.8 vol\% (12 wt\%) of clay addition [24].

Ring-opening polymerization was further applied to lactones and lactides to produce polymer/clay nanocomposites [25]. In particular, Jérôme et al. reported the intercalative polymerization of ε-caprolactone between silicate layers in the presence of supercritical carbon dioxide [26]. This dry process enables a complete exfoliation of clay platelets in the matrix, resulting in improved thermo-mechanical properties. The clay used is preferably organomodified with methyl hydrogenated tallow bis-2-hydroxyethyl ammonium ion to ensure chemical grafting between the polymer chains and the silicate layers.

Fig. (2). Schematic representation of Bragg’s law.

Besides polyamide and aliphatic polyesters nanocomposites, other matrices were synthesized via the in situ method, among which epoxy resins. In 1998, two groups published patents on layered silicate-epoxy nanocomposites. Pinnavaia and coworkers described the polymerization of a liquid epoxy resin, such as diglycidyl ether of bisphenol A (DGEBA), in the presence of a curing agent, for example polyetheramine and an organoclay [27, 28]. They demonstrated the relationships between the chain length of the onium exchange ion,
the extent of epoxy-resin intercalation and the tensile properties of the resin-clay composite. The hydrophobicity of the clay gallery surface is indeed controlled by the chain length of the alkylammonium cations and the extent of the epoxy resin intercalation into the clay is dependent on the hydrophobicity of the interlayer region. Longer linear alkyl chains (C18) facilitate the formation of the nanocomposite. Giannelis et al. used ammonium salts where one alkyl chain contains a functional group capable of reacting and bonding with the epoxy upon crosslinking, such as hydroxy, epoxy or carboxylic functional groups [29]. This results in direct attachment of the epoxy matrix to the silicate layers, thereby maximizing adhesion between the two phases and yielding a good dispersion.

Another published method involved the ionic exchange of clay with an acrylic monomer followed by the polymerization of the acrylic resin. In one example, a quaternary ammonium salt of dimethylenaminocrylamide was ion-bonded to silicate layers, while ethyl acrylate and acrylic acid were copolymerised in the clay gallery [9]. Onium ions derived from acrylic oligomers were also used to prepare organoclays for vinyl alcohol copolymers, to reach enhanced intercalation [30].

After the intercalation of monomers inside the clay gallery, researchers studied the insertion of particular agents which provide carbon-carbon double bonds or serve as chain transfer agents for free radical polymerization reactions. Such produced organoclays can be utilized in the manufacture of thermoplastics such as polystyrene and high impact polystyrene [31]. Chain transfer agents used include thiols, for example DL-cysteine, α-methylketones, α-methylalcohols or halogen compounds and are preferably combined with classical alkylammoniums.

Finally, polyolefins may also be prepared following the in situ intercalative polymerization method. This implies intercalation of silicate layers by an olefin catalyst system, such as Ziegler-Natta or metallocene catalyst, followed by the polymerization of olefin in the presence of clay. This method was initiated by Bergman et al. who used a palladium-based complex of the Brookhart-type and managed to polymerize ethylene [32] Fig. (4). In the same field, Alexandre et al. have patented a process that does not require a previous ionic exchange of the clay, resulting in cost and time savings [33]. The hydrophilic clay is first dispersed in water, to swell the clay. After removal of the water in a freeze-drying process, the clay is contacted with an alkylaluminoxane in a non-polar solvent and then contacted with a metallocene catalyst, before the introduction of an olefin or styrene monomer. Exfoliation does occur since polymerization takes place within the interlayer. However, upon melt mixing, the polymer is expelled from the gallery due to lack of affinity [34]. The use of a reactive organoclay was brought back by Lu et al. who proposed to modify clays with a functionalized surfactant containing a chain end a polymerizable double bond [35]. In that case, the monomer is thus bonded by electrostatic interaction to the silicate layer, in the aim of preventing re-stacking and agglomeration of the clay platelets. In both cited patents, an enhancement of the mechanical properties of the polyolefin nanocomposite is reported.

in situ Intercalative polymerization, especially when carried out with clay specifically organomodified to promote polymer grafting or polymer growth from the clay surface is probably the best method to insure individual exfoliation of the clay layers in the final nanocomposite materials. However, the industrial exploitation of such processes on a large scale may face two important drawbacks which are 1°) the necessary design of the clay organomodifier adapted to the type of polymerization carried out to produce the matrix and 2°) the fact that the characteristics of the produced polymer is largely influenced by some polymerization conditions.
imposed by the presence of functional organomodified clays. Indeed, on one hand, the apparition of exfoliated clays during polymer synthesis can strongly modify the viscosity of the polymerization medium and hence, the course of the polymerization. On another hand, when an initiator or a catalyst is fixed at the surface of the clay, it will define some final properties of the prepared polymer (molecular mass, polydispersity,...) in relation to its initial concentration, its accessibility to monomer(s), its variation in activity when anchored at a surface... Therefore, these processes are mainly developed for specific application in specific markets and are far from being "universal".

**Fig. (4).** Synthesis of polyethylene nanocomposite by in situ polymerization (reproduced from [32] with permission).

**ORGANOCLAYS FOR INTERCALATION IN SOLUTION**

In this method, the layered silicate is exfoliated into single layers using a solvent in which the polymer (or a prepolymer in case of insoluble polymers such as polyimide) is soluble. Due to the weak forces that stack the layers together, the clay, preferably organomodified, disperses easily in an adequate solvent. The polymer then adsorbs onto the delaminated sheets and when the solvent is evaporated (or the mixture precipitated), the sheets reassemble, sandwiching the polymer to form, in the best case, an ordered multilayer structure [1]. This technique has been widely used for water-soluble polymers such as poly(vinyl alcohol), poly(ethylene oxide), poly(vinylpyrrolidone) or poly(acrylic acid) in aqueous solutions and with natural clays. The challenge is then to avoid reaggregation of the clay sheets [36, 37].

Other researchers performed this method in organic solvent. Jeon et al. prepared nanocomposites with nitrile-based copolymer dissolved in dimethylformamide [38]. The clay was therefore previously modified by a protonated dodecylamine, while diestearyltrimethylammonium cations were used as a clay intercalant for the production of poly(ε-caprolactone) (PCL) biodegradable composites [39]. It was nevertheless found that intercalation of PCL in that organoclay does not occur largely in the PCL clay blends prepared using the solvent-cast method. Accordingly, reviewing this "intercalation in solution" method, Alexandre and Dubois note the importance to find the right layered clay, organic modifier and solvent for each polymer [1].

The Toyota research group used this technique to produce polyimide. In that case, the polymerization solvent used for polyamic acid (a precursor of polyimide) is dimethyl acetamide (DMAC). They found that clay ion-exchanged dodecyl ammonium ions could be homogeneously dispersed in DMAC [40]. A suspension of this organophilic clay and DMAC was added to a DMAC solution of polyamic acid. The film was cast from the resulting homogeneous mixture of clay and polyamic acid, and was heated at 300°C to yield a polyimide clay nanocomposite film with an exfoliated structure. In consequence, excellent gas barrier properties are obtained, with a reduction of permeability to water and to carbon dioxide of 50% upon addition of 2 wt% of clay [41].

Although a relatively large number of results are reported in the literature, very few patents can be found regarding nanocomposites prepared through intercalation in solution. This could be explained by the difficulty to transfer such polymerization to an industrial scale. Exceptions include reports on emulsion polymerization. For example, Goodyear researchers have patented the preparation of nanocomposites by addition of a water suspension of layered silicate to an aqueous emulsion of anionic elastomer particles. Subsequently, a cationic
polymeric quaternary amine or ethylene polyamine is added to the mixture to intercalate and at least partially exfoliate the water swelled clay particles by an ionic exchange [42]. Brittain [43, 44] also reported the use of a polymerizable surfactant as organic clay modifier while Weng [45], Lin [46] and Choi [47] used natural clay. In the case of water emulsion polymerization, the use of organoclays is thus not essential to ensure a fine dispersion of silicate layers.

**ORGANOCLAYS FOR MELT INTERCALATION METHOD**

Since Giannelis et al. [48] discovered that it was possible to melt-mix polymers with clay without the use of organic solvents, the high promise for industrial applications has motivated vigorous research [49]. In the melt intercalation method, the layered silicate is indeed mixed with the polymer matrix in the molten state. Except for certain polar polymers [50], a previous organomodification of the clay is in this case essential in order to obtain intercalation and/or exfoliation.

Patenting activity in this field is very diverse. While the use of alkylammonium surfactants has become common practice, several groups dedicate their research to the development of heat resistant organoclays [51-53], others make efforts to facilitate the exfoliation by incorporating two or more intercalants [54, 55] or polymeric ammonium [56] and some seek solutions for very specific applications such as improved flame retardancy [57].

The ionic exchange of organoclays with alkylammonium cations is usually done in water or in a mixture of water and ethanol [48]. International suppliers of such organoclays include Southern Clay Products Inc. (Rockwood Additives Limited), Nanocor (AMCOL International Corporation), Laviosa Chimica Mineraria, Kunimine Japan and Elementis Specialties Inc [58]. In most described cases, the clay is ion-exchanged up to 100% of its cation exchange capacity, i.e. all the gallery inorganic cations are replaced by organic cations. However, Pinnavaia et al. proposed the formation of a hybrid mixed organic-inorganic ion form of a 2:1 layered silicate in order to reduce the cost of organoclays [59]. To achieve uniform intercalation properties of these partially exchanged clays, attention has to be paid to the homo-structured gallery distribution of inorganic ions and organic ions. Other examples of partial exchange can be found in the literature [60].

Besides the high cost of alkylammonium ions, an important inconvenient is their poor thermal stability. Authors including Onikata [61], Chaiko [62] and Roelofs [63] propose solutions such as respectively the addition of an antioxidant (phenol-, sulfur-, phosphorus- or amine-based antioxidant) at 0.1-1.0 wt% of the organoclay, the use of novel quaternary phosphonium and pyridinium salts and the use of synthetic organically-modified layered silicates having built-in surfactants. The early degradation of ammonium salts particularly affects halogenated matrices such as poly(vinyl chloride). Therefore, patents are especially dedicated to the preparation of nanocomposites with this matrix. For example, Elementis Speciality researchers have developed organoclays based on combinations of silicate and tri- and tetra-[poly]oxyalkylene quaternary ammonium compounds and the ether and ester derivatives thereof [64], whereas researchers from Laviosa Chimica Mineraria have made use of quaternary ammonium ethoxylate [65] Fig. (5).

**Fig. (5). Example of structures of polyoxyalkylene(a) and ethoxylate (b) ammonium compounds.**

In order to enlarge the surfactant range to non-water soluble organic modifiers, the group of Stassin et al. developed a process for modifying natural clay in supercritical carbon dioxide [66]. In this green solvent, ammonium salts as well as siliconated ammonium compounds, highly fluorinated ammonium compounds,
phosphonium salts and sulfonium salts may be used as organic modifiers. The particularity of this process is that it is a dry method, circumventing the tedious drying procedure associated with conventional solvents. Moreover, the process is easy to transfer to the industrial scale.

Finally, the greatest challenge of organoclays remains the difficulty to reach complete exfoliation. Therefore, the use of a boosting additive was proposed by Abecassis, more specifically the use of organic diphosphates [67]. These are liquid at room temperature and can be blended mechanically with the clay in the dry form. With the addition of 0.5 wt% of diphasphate, an additional exfoliation of quaternary amine treated organoclays in polyolefin from 10% to 30% is obtained, resulting in improved mechanical properties. In another example, a clay/organic salt/organic acid complex was put forward [54]. The water swollen clay is mixed with an alkali salt of a fatty acid and heated to 50°C. A soluble polar organic acid is then added to form hydrogen bonds with the clay/organic salt complex. The first intercalant (organic salt) is prepared by heating a mixture of fatty acid and alkali base, whereas the second intercalant (organic acid) has a long carbon chain and polar carboxylic groups. In order to further expand the clay layers, the acid is preferably a macromolecule, such as polyacrylic acid. Other authors previously reported the use of water-soluble polymers to enlarge the gallery of layered silicates, either non ionic polymers [68, 69] (polyethylene glycol and similar structures), ionic polymers [70-72] (polyacrylate and related structures) and even copolymers [73]. While enhanced hydrophobicity and thermal stability is obtained for these polymer-modified clays, their preparation at a large scale may become fastidious work.

Fig. (6). Polymerization of ε-caprolactone in the presence of sc CO₂ (reproduced from [26] with permission).

All these organoclays are intended for blending with polymers via the melt intercalation method. The extensive range of thermoplastics already used to prepare nano-composites in this way can be found in previously cited reviews [1, 9, 17]. The highest advantage of melt intercalation methods lies in the fact that it gives access to a wide variety of parameters to play with in order to improve clay intercalation and exfoliation, starting from the choice of the clay organomodifier, then playing on the process parameters (shear, temperature, residence time,...) then using external additives modifying the clay polymer interaction, while working with commercially available matrices. However, reaching a high level of exfoliation remains difficult for a large variety of polymer matrices and therefore, researchers and industrials have also explored other “combined” processes such as the masterbatch approach.

POLYMER/ORGANOCLAY MASTERBATCHES

Polymer/clay masterbatches are polymer blends with a high weight content of clay prepared via either melt mixing, in situ polymerization or the intercalation in solution method. These concentrated blends are then redispersed (diluted) into polymer matrices. Pre-exfoliated masterbatches are commercialized by various suppliers including PolyOne, Nanocor and RTP Company [58].

The patenting activity in this field reveal examples from the three methods: in situ polymerization to prepare masterbatches is illustrated by Jérôme et al. [26], who prepared an aliphatic polyester nanocomposite by ring-opening polymerization in the presence of supercritical carbon dioxide Fig. (6). That unique medium allows to reach a high clay loading in the masterbatch and the product obtained after depressurization is an easily recoverable powder [74].

Secondly, the intercalation in solution method is illustrated by Lee et al., who reported the preparation of a masterbatch by dissolving polystyrene in a solvent such as xylene and then mixing the solution with
montmorillonite [75]. Thirdly, Amcol International Corp. researchers have applied the melt mixing method to prepare maleic anhydride-modified polypropylene/clay concentrates in pellet form [76]. These masterbatches are used for mechanical improvement and for flame retardation. Their particular advantage is to ease the processability, compared to the use of clay powder but also the opportunity to prepare, through these masterbatches, materials whose layered structure is already destroyed or weakened, previously to their dispersion/dilution in the final polymer matrix.

CURRENT & FUTURE DEVELOPMENTS

To conclude, this review tends to demonstrate the wide variety of organoclays available in the labs and on the market. In general, organoclays are prepared for specific polymer matrices and their choice depends on the desired application. The authors presume that future research will continue in each of the detailed methods in order to increase the number of organoclays on the market. However, industrial incorporation of organoclays will be mainly driven by melt blending process, the most operational method, especially in the form of masterbatches or with addition of compatibilizers. These may have a crucial role for matrices such as polyolefins, due to their lack of affinity for organoclays, or poly(vinyl chloride) to avoid its clay-catalysed degradation.

The importance of chemical grafting of polymer chains onto the layered silicate is to be underlined to favour the complete exfoliation via the \textit{in situ} intercalation method. This approach is nevertheless closely linked with the polymerization technique and must be developed in accordance with the particular desired matrix whereas the intercalation in solution is probably the less industrially preferred method, except for cross-linked polymers or polymers that cannot be melted.

Finally, the screening of new organoclays for industrial application will also depend on the capacity to produce these on a large scale. Besides the classical water process, supercritical carbon dioxide appears to be an excellent alternative.

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REFERENCES


