PART A: PATENTING ACTIVITY IN MANUFACTURING ORGANOCLAYS FOR NANOCOMPOSITE APPLICATIONS

1 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 1 nm and the lateral dimensions may vary from 30 nm to several microns and even larger depending on the particular silicate\textsuperscript{1,2}. 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 Al\textsuperscript{3+} replaced by Mg\textsuperscript{2+} or by Fe\textsuperscript{2+}, or Mg\textsuperscript{2+} replaced by Li\textsuperscript{+}), negative charges are generated and are counterbalanced by mono- or divalent cations located in the interlayer (Figure 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\textsuperscript{3}. 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 alkylamines, resulting in the formation of organically modified clays, also called organoclays.
These organoclays have found a large market providing thickening or rheologic properties to an increasingly wide variety of liquids including paints, coatings, inks, adhesives and similar products. Patents in this field reveal efforts to enhance the dispersibility of organoclay gellants or their biodegradability. Another example of application of organoclays is the purification of oil-contaminated water. 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. This patent published in 1950 teaches the use of organically modified bentonites (phylllosilicate from the 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 stacks. Such a poor dispersion of the silicate minerals could improve material rigidity, but certainly sacrificed the elongation at break and the toughness of the materials.

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. This invention was followed by a number of patents from TCRD between 1987 and 1990, demonstrating the use of organoclay additives for plastics, for example to replace steel components in automobiles.

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. A first one is the \textit{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 ionic 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 literature1,2,10,12-15.

In this part of the review, we will focus on the manufacturing of organoclays, 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.

2 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 advance12. 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 interplanar distance $d$ (Figure 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\textsuperscript{13}. 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).

![Figure 2. Schematic representation of Bragg’s law](image)

Montmorillonite, the natural clay mineral 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\textsuperscript{14}. 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). That was the first example of an industrial clay-based polymer nanocomposite (Figure 3).

![Figure 3. Schematic diagram of polymerization to NCH (reproduced from\textsuperscript{10} with permission)](image)

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\textsuperscript{15}. 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\textsuperscript{16}.

Ring-opening polymerization was further applied to lactones and lactides to produce polymer/clay nanocomposites\textsuperscript{17,18}. In particular, Jérôme \textit{et al.} reported the intercalative polymerization of \(\varepsilon\)-caprolactone between silicate layers in the presence of supercritical carbon dioxide\textsuperscript{19}. 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.

Besides polyamide and aliphatic polyesters nanocomposites, other matrices were synthesized via the \textit{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\textsuperscript{20,21}. 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 controlled by the chain length of the alkylammonium cations and determines the extent of the epoxy resin intercalation into the clay. Longer linear alkyl chains (C18) facilitate the formation of the nanocomposite. Giannelis \textit{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\textsuperscript{22}. 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 dimethylaminoacrylamide was ion-bonded to silicate layers, while ethyl acrylate and acrylic acid were copolymerised in the clay gallery\textsuperscript{10}. Onium ions derived from acrylic oligomers were also used to prepare organoclays for vinyl alcohol copolymers, to reach enhanced intercalation\textsuperscript{23}.

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\textsuperscript{24}. Chain transfer agents used include thiols, for example DL-cysteine, $\alpha$-methylketones, $\alpha$-methylalcohols or halogen compounds and are preferably combined with classical alkylammonium cations. Free radical initiators with positively charged head group such as two-step procedure\textsuperscript{25}.

Finally, polyolefins may also be prepared following the \textit{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 \textit{et al.} who used a palladium-based complex and managed to polymerize ethylene\textsuperscript{26} (Figure 4). In the same field, Alexandre \textit{et al.} have patented a process that does not require a previous ionic exchange of the clay\textsuperscript{27}. 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\textsuperscript{28}. The use of a reactive organoclay was brought back by Lu \textit{et al.} who proposed to modify clays with a functionalized surfactant containing as a chain end a polymerizable double bond\textsuperscript{29}. 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.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure4}
\caption{Synthesis of polyethylene nanocomposite by \textit{in situ} polymerization (reproduced from\textsuperscript{26} with permission)}
\end{figure}

In \textit{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 organoclays. Indeed, on one hand, the appearance 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 such as molecular mass and polydispersity, in relation to its initial concentration, its accessibility to monomer(s) or 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”.

3 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. 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.

Other researchers performed this method in organic solvent. Jeon et al. prepared nanocomposites with nitrile-based copolymer dissolved in dimethylformamide. The clay was therefore previously modified by a protonated dodecylamine and was partially exfoliated according to XRD and TEM analysis. Distearyldimethylammonium cations were used as a clay intercalant for the production of poly(ε-caprolactone) (PCL) biodegradable composites. Nevertheless, it was found that intercalation of PCL in that organoclay does not occur largely in the 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.

The Toyota research group used this technique to produce polyimide. In that case, the polymerization solvent chosen 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. 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.

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 system 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. Brittain W. J. also reported the use of a polymerizable surfactant as organic clay modifier while Weng W., Lin K.-F. and Choi Y. S. 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.

4 Organoclays for melt intercalation method

Since Giannelis and his coworkers 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. In the melt intercalation method, the layered silicate is indeed mixed with the polymer matrix in the molten state. Except for certain polar polymers, 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\textsuperscript{46-51}, others make efforts to facilitate the exfoliation by incorporating two or more intercalants\textsuperscript{52,53} or polymeric ammonium\textsuperscript{54,55} and some seek solutions for very specific applications such as improved flame retardancy\textsuperscript{56,57}.

The ionic exchange of organoclays with alkylammonium cations is usually done in water, or in a mixture of water and ethanol\textsuperscript{43,58}. 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\textsuperscript{59}. 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 \textit{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\textsuperscript{60}. To achieve uniform intercalation properties of these partially exchanged clays, attention has to be paid to the homostructured gallery distribution of inorganic ions and organic ions.

Besides the high cost of alkylammonium ions, an important inconvenient is their poor thermal stability. Different solutions are proposed, such as the addition of an antioxidant (phenol-, sulfur-, phosphorus- or amine-based antioxidant) at 0.1-1.0 wt\% of the organoclay\textsuperscript{61}, the use of novel phosphonium\textsuperscript{46-48}, pyridinium\textsuperscript{49} or imidazolium salts\textsuperscript{50} as organomodifiers, or the use of synthetic organically-modified layered silicates having built-in surfactants\textsuperscript{51}. 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 Specialty 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\textsuperscript{62}, whereas researchers from Laviosa Chimica Mineraria have made use of quaternary ammonium ethoxylate\textsuperscript{63} (Scheme 1).
Scheme 1. Example of structure of polyoxyalkylene (a) and ethoxylate (b) ammonium compounds

In order to enlarge the surfactant range to non-water soluble organic modifiers, the group of Jérôme and coll. developed a process for modifying natural clay in supercritical carbon dioxide\textsuperscript{64}. In this green solvent, ammonium salts as well as silicone 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.

Finally, the greatest challenge of organoclays remains the difficulty to reach complete exfoliation. Therefore, the use of a boosting additive was proposed by Abecassis D., more specifically the use of organic diphosphates\textsuperscript{65}. 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 diphosphate, 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\textsuperscript{52}. The water swollen clay is mixed with an alkali salt of a fatty acid and heated to 50\textdegree 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\textsuperscript{66,67} (polyethylene glycol and similar structures), ionic polymers\textsuperscript{68-70} (polyacrylate and related structures) and even copolymers\textsuperscript{71}. While enhanced hydrophobicity and thermal stability is obtained for these polymer-modified clays, their preparation at a large scale may become fastidious work.
All these organoclays are intended for blending with polymers via the melt intercalation method. The extensive range of thermoplastics already used to prepare nanocomposites in this way can be found in previously cited reviews\textsuperscript{1,2,10}. 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.

5 Polymer/organoclay masterbatches

Polymer/clay masterbatches are polymer blends with a high weight content of clay prepared via either melt mixing, \textit{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\textsuperscript{59}.

The patenting activity in this field reveal examples from the three methods: \textit{in situ} polymerization to prepare masterbatches is illustrated by Jérôme \textit{et al.}, who prepared an aliphatic polyester nanocomposite by ring-opening polymerization in the presence of supercritical carbon dioxide (Figure 5)\textsuperscript{19}. That unique medium allows to reach a high clay loading in the masterbatch and the product obtained after depressurization is an easily recoverable powder\textsuperscript{72}.

\textbf{Figure 5.} Polymerization of $\varepsilon$-caprolactone in the presence of sc CO\textsubscript{2} (reproduced from\textsuperscript{19} with permission)
Secondly, the intercalation in solution method is illustrated by Lee S. M. 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\textsuperscript{73}. Thirdly, Amcol International Corp. researchers have applied the melt mixing method to prepare maleic anhydride-modified polypropylene/clay concentrates in pellet form\textsuperscript{74}. 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.

6 Current and 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.
PART B: ORGANOCLAYS WITH THERMALLY STABLE ONIUMS

1 Introduction

As detailed in the first part of this literature review, polymer/clay nanocomposites can be synthesized in a number of ways, but an organic treatment is often needed to ensure compatibility between the hydrophilic clay and the usually hydrophobic polymer. The most commonly used organic treatment to manufacture organoclays today is ionic exchange with alkylammonium salts. On the other hand, the preparation of polymer/clay nanocomposites via the melt blending method and/or their subsequent processing (irrespective of the preparation method) requires elevated temperatures. If the processing temperature is greater than the thermal stability of the organic treatment in the clay layers, decomposition will occur, releasing undesirable compounds and altering the interface between the filler and polymer.

To deal with this issue, Xie et al. studied the thermal degradation chemistry of alkyl quaternary ammonium montmorillonite\textsuperscript{75,76}. They determined an onset temperature of organoclays decomposition of approximately 155°C via thermogravimetric analysis (TGA) and 180°C via TGA coupled with mass spectrometry (TGA-MS) where TGA-MS enables the differentiation of water desorption from true organic decomposition. Analysis of products (GC-MS) indicated that the initial degradation of the surfactant in montmorillonite (MMT) follows a Hofmann elimination reaction (Figure 6) and that the architecture (trimethylalkyl or dimethyldialkyl), chain length, surfactant mixture, exchanged ratio or preconditioning (washing) does not alter the initial onset temperatures. They also showed that catalytic sites on the MMT layer reduce thermal stability of the surfactants by an average of 15-25°C relative to the parent alkylammonium salt.

![Figure 6](image)

**Figure 6.** Hofmann degradation of an alkylammonium organic treatment: the beta hydrogen on the alkyl group is eliminated, giving an alpha olefin, a free amine and an acidic proton (adapted from\textsuperscript{77})
Further detailed characterization of the thermal degradation of several commercial (from the Cloisite® type, presented in Table 1) and experimental organoclays was reported by Paul and his coworkers. They suggested via NMR data that ammonium surfactants decompose primarily via nucleophilic attack of chloride anions; however, if the residual chloride anions are completely removed from the organoclay, primary degradation pathway switches to a Hofmann elimination reaction. In contradiction with Xie et al., they found that the chemical structure of the surfactant plays an important role in their thermal degradation. In this way, the presence of an aromatic residue leads to a less stable organoclay. From both groups’ studies, we may consider that the onset temperature of degradation of ammonium-modified clays is comprised between 160 and 210°C.

**Table 1.** Most common clays from the Cloisite® type (HT is hydrogenated tallow: ~65% C18, ~30% C16, ~5% C14)

<table>
<thead>
<tr>
<th>Commercial name</th>
<th>Organomodifier</th>
<th>Weight loss on ignition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cloisite® Na⁺</td>
<td>-</td>
<td>0 %</td>
</tr>
<tr>
<td>Cloisite® 10A</td>
<td>Cl⁻NH⁺CH₃⁺CH₂⁺HT</td>
<td>39 %</td>
</tr>
<tr>
<td>Cloisite® 15A</td>
<td>Cl⁻NH⁺HT</td>
<td>43 %</td>
</tr>
<tr>
<td>Cloisite® 20A</td>
<td>Cl⁻NH⁺HT</td>
<td>38 %</td>
</tr>
<tr>
<td>Cloisite® 30B</td>
<td>Cl⁻NH⁺CH₂CH₂OH</td>
<td>30 %</td>
</tr>
<tr>
<td>Cloisite® 93A</td>
<td>Cl⁻NH⁺HT</td>
<td>37.5 %</td>
</tr>
</tbody>
</table>

The limited thermal stability of ammonium organomodifiers in MMT has several negative effects on nanocomposite materials. The degradation of both alkylammonium and polyamide-6 (PA-6) itself during processing in the presence of nanodispersed MMT was demonstrated by NMR spectroscopy. It was found that as much as 80 % (±10 %) of the quaternary ammonium (dimethyl-di(hydrogenated tallow)ammonium) had degraded in the samples with extrusion times long enough to give delaminated nanocomposites, meaning that the
nanocomposite was contaminated with up to 3 wt% tertiary amine. Alkylammonium cations degradation upon compounding can reduce molecular mass of PA-6\textsuperscript{81}, limit the extent of intercalation and/or exfoliation in polyolefin matrices\textsuperscript{82} or induce pronounced color formation in polyvinyl chloride (PVC)\textsuperscript{83,84} or polycarbonate (PC)\textsuperscript{85}. Moreover, Frankowski \textit{et al.} reported chain scission of polystyrene (PS) containing organomodified MMT after relatively short annealing times in an O\textsubscript{2}-rich environment, whereas branching and cross-linking are prevalent after long exposure times\textsuperscript{86}.

With particular regard to flame retardancy, the organic treatment degradation is a very important issue as the decomposition can cause a quick release of fuel early in the ignition process and make the nanocomposite easier to ignite than the pure polymer\textsuperscript{77,87,88}. Note that this explanation is nevertheless not accepted by the whole community of fire scientists. Some propose alternative causes for the decrease of ignition times in organoclay-based nanocomposites, such as the modification of the molten medium viscosity and ability to dissipate heat\textsuperscript{89}.

In order to overcome these limitations, various more thermally stable cationic surfactants have been proposed as alternative routes to alkylammonium modifiers. This part of the review will detail the use of the most promising imidazolium and phosphonium salts, with the emphasis on most significant properties improvement of the nanocomposites incorporating these.

2 Organoclays with imidazolium salts

The use of new thermally stable imidazolium-treated layered silicates for the preparation of nanocomposites was first reported by Gilman \textit{et al.}\textsuperscript{90,91}. They treated sodium montmorillonite with various dimethylalkylimidazolium salts via standard literature ionic exchange methods. TGA data of imidazolium organoclays, recorded under nitrogen atmosphere, showed an improvement in thermal stability of 40 to 60°C for these organoclays compared to dimethyl-dioctadecylammonium MMT. A complete study of thermal degradation of alkylimidazolium salts was published separately\textsuperscript{92}. The enhanced thermal stability of imidazolium halides compared to ammonium halides has been reported to be due to the delocalization of the positive charge over the imidazole ring. The structures of imidazolium salts used for the modification of MMT clay, the corresponding host matrix and properties studied are summarized in Table 2.
Two matrices were tested in a first attempt to prepare nanocomposites with imidazolium organoclays. Polystyrene (PS) was melt blended with decyl- and hexadecyl-functionalized imidazolium MMTs (DDMIM-MMT and DMHDIM-MMT). However, a poor miscibility was
observed, a microcomposite was obtained with the former and partial intercalation with the latter. DMHDIM-MMT was extruded with PA-6 leading in this case to an exfoliated nanocomposite.

Other researchers proposed the use of benzimidazolium salts to modify clays. BI-MMT (see Table 2 for the structure) has an onset degradation temperature of 40°C higher than that measured for Cloisite® 20A. When melt blended with PS, ABS (acrylonitrile-butadiene-styrene copolymer) and HIPS (high impact PS), this organoclay led to the formation of intercalated nanocomposites with good overall dispersion. Enhanced thermal stability and improved fire properties were reported. Nevertheless, a shorter ignition time compared to the matrix alone was observed, as is the case with ammonium-modifiers. The maximum reduction in peak heat release rate (PHRR) was of 36 % for PS, which is similar to the result of PS melt blended with Cloisite® 20A (PHRR reduction of 38 %).

The effect of thermally stable imidazolium treated MMT on the gas permeation and mechanical behavior of polypropylene (PP) nanocomposites was studied by V. Mittal. He synthesized an imidazolium salt with 2 long alkyl chains to favor clay platelets separation and prepared composites with different volume fractions of organoclay by melt intercalation. The oxygen relative permeability decreased substantially with increased volume fraction. A decrease of 45 % was noted with 4 vol% filler fraction. In comparison, a maximum decrease of 35 % was reported with composites containing the same volume fraction of dimethyldioctadecyl-(2C18) ammonium modified clay. Tensile modulus linearly increased with filler content while yield stress decreased due to the lack of strong interfacial interactions and the presence of clay stacks. A mostly intercalated morphology was depicted, similar as that obtained with 2C18 ammonium-clay. It must be noted that no compatibilizer was used in this study, which is usually the case with PP nanocomposites.

Poly(ethylene terephthalate) (PET) is another widely used polymer, wherein clay dispersion is far from trivial. This is mainly due to the poor compatibility between PET and organic modifier residing in commercial organoclays as well as to its very high melt processing temperature (~280°C). Therefore, several groups studied the possibility of using thermally stable organoclays in this matrix. Among them, Kim et al. proposed a different kind of imidazolium salt, namely with a hydroxyl group (see Table 2). After melt blending of PET with this imidazolium-organoclay, a homogeneous dispersion of clay stacks was
observed by TEM, with thinner remaining clay stacks compared to Cloisite® 15A and Cloisite® 30B. Most interestingly, the nanocomposite showed an enhanced tensile modulus without sacrifice on the yield stress and elongation at break. This was attributed both to improved thermal stability of organomodifier and better interaction with the matrix.

Finally, imidazolium-modified clays were also used for the in situ preparation of nanocomposites. Examples were found with polycondensation reactions to prepare PET\textsuperscript{100} or PC\textsuperscript{101} nanocomposites and free radical polymerization of styrene monomer\textsuperscript{97}. For the latter, Bottino et al. prepared reactive imidazolium salts, namely containing a vinyl group (cfr Table 2). A mixed intercalated-exfoliated morphology was observed. The quality of dispersion is enhanced compared to the reference sample containing C18-ammonium but inferior to polystyrene nanocomposites obtained in situ with a N,N-dimethyl-n-hexadecyl-(4-vinyl-benzyl)ammonium (VB16), according to quantitative analysis of extent of exfoliation by NMR\textsuperscript{108}. The mechanical properties were not reported.

As closing remarks, only a few imidazolium salts are commercially available. Surfactants with one or two long alkyl chain can be easily synthesized from various imidazole compounds. The obtained salts usually present sufficient solubility in water to use the classical ionic exchange procedure. However, the search for enhanced compatibility with specific polymers leads to multi-step synthesis of particular imidazolium salts, requiring organic solvent such as dimethylsulfoxide, diethylether or tetrahydrofuran for successful clay modification, which renders the process less environmentally friendly.

3 Organoclays with phosphonium salts

Phosphonium salts are the second most studied thermally stable onium salts. Their thermal stability was studied by Xie et al. in the same way as their parent ammonium-MMT\textsuperscript{109}. They showed that the onset decomposition temperature ranged from 190°C to 230°C. The interlayer environment of the MMT has a more severe effect on stability of the phosphonium surfactant than previously reported for ammonium-MMT. Nonetheless, the overall thermal stability in addition to their conventional purpose as stabilizers make phosphonium salts excellent candidates for organoclays.
Several studies focus essentially on ionic exchange of phosphonium salts in layered silicates and their thermal characterization\textsuperscript{110-113}. In these studies, surfactants of various structures, including triphenylalkyl- and tetraalkylphosphonium salts were used. Ionic exchange with triphenyl-based surfactants is done either in pure water or in a mixture of water and alcohol (methanol or ethanol). The use of tetraalkylphosphonium salts requires a less polar organic solvent such as diethyl ether. All authors concluded that these salts present a good potential for the synthesis of polymer/clay nanocomposites. However, up to now, only a few studies demonstrated this statement. In these studies, phosphonium salts were almost exclusively synthesized from triphenylphosphine. The variety of such salts effectively tested for polymer nanocomposites with the corresponding host matrix and properties studied is summarized in Table 3.

Table 3. Structures of phosphonium salts synthesized from triphenylphosphine and tested in MMT for polymer nanocomposites (X$^{-}$ is Br$^{-}$ unless specified)

<table>
<thead>
<tr>
<th>Substituent on triphenylphosphine</th>
<th>Host polymer</th>
<th>Properties</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>R = dodecyl</td>
<td>PET in situ</td>
<td>thermal, tensile</td>
<td>114</td>
</tr>
<tr>
<td>R = dodecyl/octadecyl/benzyl</td>
<td>PET</td>
<td>thermal, tensile</td>
<td>115</td>
</tr>
<tr>
<td>X = Cl in case of benzyl</td>
<td>PS</td>
<td>fire</td>
<td>77,116</td>
</tr>
<tr>
<td></td>
<td>epoxy</td>
<td>fire</td>
<td>117</td>
</tr>
<tr>
<td></td>
<td>SAN</td>
<td>fire</td>
<td>102</td>
</tr>
<tr>
<td>R = hexadecyl</td>
<td>PET in situ</td>
<td>thermal</td>
<td>100,114</td>
</tr>
<tr>
<td></td>
<td>PC in situ</td>
<td>morphology</td>
<td>101</td>
</tr>
<tr>
<td>R = octadecyl</td>
<td>PVDF</td>
<td>crystallization, tensile</td>
<td>119</td>
</tr>
<tr>
<td>R = vinylbenzyl</td>
<td>rubber</td>
<td>vulcanization</td>
<td>120</td>
</tr>
<tr>
<td>R = 2-dimethylaminoethyl</td>
<td>PMMA in situ</td>
<td>anti-corrosion</td>
<td>121</td>
</tr>
<tr>
<td>R = [\text{O} \text{H} \text{O} \text{H}]</td>
<td>PC in situ</td>
<td>thermal</td>
<td>101</td>
</tr>
</tbody>
</table>
As described above, PET is one of the challenging matrices to prepare nanocomposite. Stoeffler et al. used tributylhexadecylphosphonium bromide as clay organomodifier, in comparison with an imidazolium, a pyridinium and an ammonium salt. Phosphonium organoclay particles were well-distributed in the matrix but with a low extent of intercalation, as a result from a poor compatibility. An extensively detailed study comprising mechanical properties was performed by Patro et al. They found that benzyltriphenylphosphonium-modified clay at 3 wt% gave the best balance of mechanical properties in terms of modulus and elongation at break. Elsewhere, preparation of PET nanocomposites via in situ polycondensation revealed that catalytic substances released from MMT accelerated the degradation during processing. When a phosphonium-modifier was introduced, the total quantity of the metallic derivatives which had a catalytic activity decreased, leading to improved processing stability of PET.

Another polymer processed at high temperature is polycarbonate (PC). Rama et al. interestingly prepared a phosphonium salt with a reactive bisphenol group, that allowed the preparation of exfoliated PC/clay nanocomposites via in situ melt polycondensation at temperatures up to 290°C. This is in contrast with usual poor dispersion of layered silicate in this matrix. However, the use of thermally stable organoclays did not improve the dark coloration of the composites. This is attributed to complex degradation reactions promoted by excess basic compounds or multivalent metal ions intrinsically present in MMT.

At last, phosphonium organoclays were used to prepare nanocomposites with enhanced flame retardancy (fire properties). Studied matrices include PS, SAN and epoxy resin. In all cases, a reduction in peak of heat release rate compared to pure matrix is reported. However, in contradiction with prior assumptions, no improvement is noticed in comparison with well-dispersed ammonium organoclays. Although not explicitly stated in the cited papers, this might be explained by the insufficient degree of exfoliation obtained with phosphonium organoclay. It can be noted that only one type of phosphonium cation has been tested as organomodifier for this purpose (see Table 3).

4 Current and future developments

Thermally stable organoclays are needed in high melt temperature polymers to prevent negative effects occurring from organomodifier decomposition during compounding as well
as for good material ageing and fire properties. However, the use of thermally stable onium salts to modify layered silicates is only an emerging field. Several authors described the preparation of organoclays without reporting dispersion in polymer. Others reported the preparation of polymer nanocomposites from organoclays with enhanced stability but limited their study to morphology and thermal properties. Thus, a lot of effort has still to be done to demonstrate the potential of clay based on imidazolium and phosphonium salts. In particular, the extent of clay exfoliation has to be improved. While the choice of the appropriate preparation method (in situ or melt intercalation) has been discussed in the first part of this literature review, the selection of the right structure of organomodifier is also crucial. Restraints in this research field include the limited commercial availability of functional imidazolium and phosphonium salts, together with the poor solubility in water (classical medium of clay modification) of potentially most interesting salts. Indeed, salts with a strong hydrophobic character are more likely to enhance the compatibility of clay with non-polar polymers.

Besides, the reported catalytic activity of montmorillonite clay may also contribute to undesired matrix degradation. Other types of layered silicates (synthetic or purified MMT, hectorite, saponite, ...) should thus also be envisaged in combination with thermally stable oniums in order to produce nanocomposites with satisfactory level of exfoliation and less or no detrimental influence on the matrix integrity.
REFERENCES

Literature review

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