

Synthesis of Polymer Nanocomposites by water-assisted extrusion

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1.1 Introduction

In the large field of nanotechnology, polymer matrix based nanocomposites have become a prominent area of current research and development in order to upgrade their performances. Clays are one group of nano-fillers which have been widely used for the preparation of polymer nanocomposites. Polymer/clay nanocomposites (PCNs) are polymer reinforced with clay particles, mainly phyllosilicates, having a least one dimension in the nanometer scale. During the last decades, PCNs received a considerable scientific and technological interest mainly due to their unique combination of properties. A few percent of clay usually confer a flame retardant behavior, higher mechanical and barrier properties regarding the neat polymer [1-4]. Due to the nanoscale dispersion of the clay mineral filler, the reinforcement efficiency of the composite can be significantly better than conventional minerals fillers. The final properties of nanocomposites depend directly on several factors like the chemistry of the polymer matrix, the affinity between filler and polymer, the geometry of the particle, its degree of orientation and dispersion inside the polymer as well as the way of preparation [3,4]. Polymer clay nanocomposites technology originated in the late 1980's at Toyota's Central R&D laboratories [5]. Toyota focused mainly on nylon composite and holds the basic patents on their production [6-8]. Since this pioneering work, several books [9-11] and reviews [1,2,12-14] treat on PCNs. The attention has been also focused on the preparation method of these nanocomposites. To prepare polymeric nanocomposites, different methods have been developed, among which melt-compounding has attracted a great interest to produce polymer/clay nanocomposites. The benefits of this technique result from its cost-effectiveness, its environment-friendly aspect and also its compatibility with current industrial processes such as extrusion. The resident time and the shear created in the melt during processing may also be helpful to support the dispersion of particles. However, it is not always enough to break up big particle agglomerates, as the resulting dispersion of particles may remain poor and usually require the use of clay organomodification to improve the

intercalation and to solve the lack of compatibility between the polymer matrix and the filler. Another problem of producing PCNs concerns the thermal stability of the surfactant in the organoclay. At extrusion temperatures, the interlayer alkylammonium surfactants often decompose leading to a collapse of the silicate layers and impart undesirable colour, odour and taste to the composite [15-20]. An alternative way to prepare nanocomposites is the water-mediated melt-compounding method, where water is used as a substitute for classical alkylammonium intercalating/exfoliating agents. This technique has gained ground because of the following benefits. First, many water-dispersible commercial nanofillers are readily available. Second, the production of nanocomposites by using aqueous dispersions or slurries is not only an affordable method (no fillers' organophilic modification is needed), but it is also less hazardous to one's health. Moreover, this original process opens a novel ecofriendly route for especially the temperature-dependent reinforcement materials such as natural fibres.

1.2 Nanocomposites structure and characterization

1.2.1 Clays

Nanocomposites can be classified depending on the shape of the nanofiller. Depending on their dimensions, there is three categories of nanofillers: nanoparticles, nanotubes or whiskers and nanolayers [21]. These nanoscale particles can further be divided in three types as natural, incidental, and synthetic or engineered nanoparticles depending on their pathway.

In the synthesis of nanocomposites, the commonly used layered silicates are natural or synthetic minerals. Clays are characterized by a layered structure. Their crystal structure consists of layers made up of tetrahedral sheets in which a silicon atom is surrounded by four oxygen atoms and octahedral sheets in which a metal like aluminum or magnesium is surrounded by eight oxygen atoms. The total layer thickness is around 1 nm and the lateral dimensions of these layers may vary from 30 nm to microns or larger, depending on the particulate silicate, the source of the clay and the method of preparation [1,2,9-14,21].

Montmorillonite (MMT), hectorite and saponite are the most commonly used in the preparation of polymer nanocomposites. The generally accepted formula for MMT is $(\text{Na,Ca})_{0,3}(\text{Al,Mg})_2\text{Si}_4\text{O}_{10}(\text{OH})_2.n\text{H}_2\text{O}$. MMT is characterized by a high aspect ratio, presents a well dispersed state without breaking of layers and has a surface area of about $750\text{m}^2/\text{g}$. These benefits in addition to its ease availability make MMT widely accepted for the preparation of polymer nanocomposites.

Halloysite (HNTs), another type of clay nanofiller combining the geometry of nanotubes and the chemistry of kaolinite are recently focusing a lot of attention [22-31]. HNTs is a naturally occurring aluminosilicate ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 \cdot 2\text{H}_2\text{O}$) with a predominantly hollow tubular structure. As compared to other layered silicates, halloysite can thus be more easily dispersed in a polymer matrix due to the weak secondary interactions among the nanotubes via hydrogen bonds and van der Waals forces [30,32].

1.2.2 Organomodification of layered silicates

Improvement of polymer properties is strongly affected by the state of dispersion. But, the formation of well dispersed pristine clay layers in polymers is a challenge due to their high intrinsic hydrophilicity which make them incompatible with hydrophobic polymer. Incompatibility and weak interfacial interactions prevent the preparation of dispersed stable nanocomposite with improved properties. In their pristine state, clays are “miscible” only with few hydrophilic polymers such as poly (ethylene oxide) (PEO) and poly (vinyl alcohol) (PVA) [33-34]. In order to solve the lack of compatibility between clay layers and hydrophilic polymers, clay layers are usually organomodified. This treatment consists in a surface clay modification which can be achieved through a cation exchange process by the replacement of sodium and calcium cations present in the clay galleries by alkylammonium or alkylphosphonium (onium) cations [1-4,12,14,21]. The ammonium cations is referred to as a “surfactant” owing to its amphiphilic nature. The exact effect of the surfactant concentration on the final nanocomposite structure is still a burning issue depending on the matrix nature. Some researchers believe that surfactant quantity higher than the cation exchange capacity (CEC) of the clay reduces the miscibility between the polymer and the inorganic mineral during nanohybrid synthesis. Indeed, they showed that the presence of excess modifier in the organoclay gives undesirable effects on nanocomposite properties [35-38]. Whereas, Ratnac et al. [36] reported that the excess of amphiphilic substance, improves the dispersion level of silicate layers in bulk-polymerized poly(methyl methacrylate) nanocomposites.

The main problem in preparing polymer/clay nanocomposites concerns the thermal stability of the surfactant in the organoclay. The interlayer alkylammonium surfactants often decompose at extrusion temperatures by the so-called Hoffmann elimination leading to a collapse of the silicate layers and limiting the composite properties [15-20]. Moreover, the aforementioned decomposition products impart undesirable colour, odour and taste to the composite [15-20]. Efforts have been made to synthesize more thermally stable organoclays

using other cationic surfactants. For example pyridinium and quinolinium [39], imidazolium [40], phosphonium [41] and stibonium [42] salts were used. Organoclays synthesized from these surfactants are more thermally stable, but unfortunately, these surfactants are expensive and/or require multistep synthesis limiting large-scale production. Nowadays, the related research is mostly fueled by two aspects: the replacement of organophilic layered silicates by pristine ones in order to avoid this expensive chemical modification of nanofillers and the development of harmless, environmentally friendly production methods. The greatest interest has involved melt processing, especially water-assisted extrusion (using untreated and even organomodified clays), which is generally considered more economical, more flexible for formulation, and involves compounding and fabrication facilities commonly used in commercial practice [43-78]. This point will be discussed later in section 1.3.3.2.

1.2.3 Nanocomposites structure and characterization

Depending on the way of preparation and of the nature of the components, three types of composites can be prepared when working with clay and polymers (Figure 1.1) [1-4,12,14]. Three main classes of nanocomposites can be obtained and are referred as: immiscible (conventional or microcomposite), intercalated and miscible or exfoliated. In the immiscible structure, the silicate layers are dispersed in the polymer matrix in the form of particles including tactoids or aggregates of tactoids as they were in the clay powder because the platelets are not separated. Intercalated structures are obtained when single polymer chains are intercalated between the silicate layers with their regular alternation and laminae [1,14]. In the miscible or exfoliated hybrids, the clay layers are well delaminated and individually dispersed in the polymer matrix. In this case, the order's structure is lost and the interlayer distance is comparable to the radius of gyration of the polymer. The exfoliation or delamination configuration is the desired morphology because it maximizes the polymer-clay interactions by rendering the entire layers' surface available by the polymer and therefore leads to the most significant improvements of mechanical property [1-4,12,14].

Structural characterization of nanocomposites has primarily centered around two complementary techniques: X-ray Diffraction (XRD) and Transmission Electron Microscopy (TEM) [3,14,59,65,67,69,70,73,74,76]. Complementary techniques such as rheology, Differential Scanning Calorimetry (DSC) [19,20,21,23,31,68,75,77,87], Thermogravimetric

Analysis (TGA) [23,28,75,77] and solid state nuclear magnetic resonance (NMR) [79-81] are also used to provide information about the structural analysis of nanocomposites.

1.3 Nanocomposites preparation

The preparative methods are divided in three main groups according to the processing techniques: *Intercalation from solution*, *in situ polymerization* and *melt compounding*. The present work focuses on the melt intercalation, especially the melt blending with the aid of water.

1.3.1 Intercalation from solution

This technique is based in using a solvent in which the polymer is soluble and the filler can be easily dispersed. The final step consists of removing the solvent, either by vaporization, usually under vacuum, or by precipitation. This method has been widely used and from a long time in the case of water soluble polymers like PVA [82,83], PEO [84-90], epoxy [91], polyethylene glycol (PEG) [94], poly(methyl methacrylate) (PMMA) [93], or not like nylon 6 (PA6) [95] and many other nanocomposites especially based on HNTs [96-101]. Aromatic solvents such as xylene or toluene are generally used to dissolve polyolefin [102-104] and epoxy [92].

However, from an industrial point of view, this method is not suitable due to the large amount of organic solvent required which are always environmentally unfriendly and economically prohibitive.

1.3.2 In situ polymerization

In situ polymerization is a two-step process. The nanoparticles are first dispersed in a monomer solution and the resulting mixture is polymerized using standard polymerization methods. The driving force of this technique is the polarity of the monomers. In situ polymerization was the first method used to synthesize polymer–clay nanocomposites based on PA6. The preparation of PA6 nanocomposites by in situ polymerization has been first reported by the Toyota research group [5,105,106]. Further studies have also shown that PA6 chains are bonded to the silicate layers, which acts as a cross-linker and restricts their motion [107-108]. Reichert et al. [109] reported for PA12 nanocomposites that the structure was

found to be partially exfoliated and intercalated. In the case of PA1012 nanocomposites, Wu et al. [110] obtained an exfoliation structure.

An appropriate catalyst is needed to polymerize polyolefins between the clay layers. Ziegler-Natta catalysts can be used but generally metallocene catalysts are employed because they are more tunable [111-113]. In the case of HNTs, only few polymer-halloysite nanocomposites have been prepared via in situ polymerization [114,115].

In situ polymerization has proved successful in the preparation of various polymer-layered silicate nanocomposites, but this technique has also shown important drawbacks: (1) it is a time-consuming preparation route, the polymerization reaction may take more than 24 h; (2) the platelets may re-aggregate during subsequent processing steps because exfoliation is not always thermodynamically stable; (3) the process is available only to the resin manufacturer who is able to dedicate a production line for this purpose [116].

1.3.3 Melt compounding

Melt blending is the standard preparative method for PCNs. The polymer is melted and combined with the desired amount of layered silicate in an extruder, internal, kinetic energy or continuous mixer. There are several advantages to the melt route compared to the polymerization route. The process is more economic, it's better suited for rapid change in formulation and in industry, it does not require a polymer production line dedicated to that sole product. At the same time, melt processing is environmentally benign among all the methods of preparing polymer-clay nanocomposites since no solvents are required. The melt process can be divided into static and dynamic processes. Dynamic intercalation is the more conventional compounding operation performed in a processing equipment. During shearing, polymer chains diffuse from the bulk polymer melt into the galleries between the silicate layers, as shown in Figure 1.2. Thus, several thermoplastic polymers, including PA [18,24,35,43,44], poly(ethylene terephthalate) (PET) [40,78], ethylene-vinyl acetate (EVA) [50,117], PA12 [26], PA11 [77], polyolefins [32,45-49,52-54,62,75], PLA [38,118-120], etc., have been used to study nanocomposite preparation by melt intercalation.

1.3.3.1 Melt blending of polymer /organoclay nanocomposites

In 1999, Liu et al [121] broke new ground in applying the melt compounding technique for the preparation of a commercially available PA6/organomodified MMT (o-MMT) nanocomposite using a twin-screw extruder. Since that time, this route has been widely

studied during the past years. Cho and co-workers [122] showed that it was possible to obtain exfoliated nanocomposites comparable to those produced by in situ polymerization, using a twin screw extruder. This exfoliation results of the combination of optimal processing conditions and good polymer organoclay affinity. Dennis et al. [123] prepared PA6 nanocomposites using different processing techniques and different processing conditions. The best delamination was observed with a medium shear intensity extruder and, from this study, the most suitable extruder was a non intermeshing one.

As polyolefins are apolar matrix, the use of a compatibilizer containing polar functions is required in addition to the organoclay. Polypropylene (PP) grafted with maleic anhydride (PP-g-MA) is usually used as compatibilizer [53,54].

It is worth noting that the exfoliation of clay in a polymer matrix does not only depend on the processing conditions but also on the structure and nature of the organic compound used to modify the clay. Fornes et al. [35,124] made an extensive study on the effect of the organo-modified clay structure on the morphology and properties of PA6 nanocomposites. The authors proposed that these effects stem from the amount of exposed silicate surface. Alkyl ammonium ions that cover a large part of the clay surface hinder the “polar-polyamide/polar clay” surface favourable interactions. This hypothesis has been further confirmed by the same group. This concept is supported by theoretical works of Tanaka et al. [125] and Fermeglia et al. [126] on the prediction of the binding energy between polyamide chains and organo-modified clay. Shorter aliphatic chains produce more favourable binding energies with respect to longer ones. Instead of using alkyl ammonium cation to organo-modify the montmorillonite, it is possible to use a new surfactant obtained through co-intercalation of an epoxy resin and an ammonium salt. Good level of dispersion were observed resulting of the strong interaction between the epoxy groups confined in the layers and amide groups of the PA6 [127]. The dispersion state of HNTs has been enhanced by adding small organic compounds containing hydrogen-bonding functionalities [128].

1.3.3.2 Melt blending of polymer /pristine clay nanocomposites

There are some disadvantages to use organophilic clays. Firstly, the organo-treatment is expensive and increases the final product cost. Secondly, the thermal degradation of organophilic clays begins generally at 180°C while the extrusion temperature for thermoplastic polymers is generally in the range of 200-250°C [15,17,19,20,129]. The surfactant degradation limits clay dispersion and consequently the composite properties [15-

20]. Moreover, surfactant decomposition products impart unhealthy and undesirable color, odor and taste to the composite [20,130]. Nowadays, the related research is mostly fueled by two aspects: the replacement of organophilic layered silicates by pristine ones and the development of harmless, environmentally friendly production methods. Furthermore, developing a new compounding technique to exfoliate unmodified silicate would reduce nanocomposites' global cost. Starting from pristine clay, it is possible to obtain nanocomposites either by modifying the clay in situ using different kinds of additives or by using actually unmodified clay.

1.3.3.2.1 In situ organomodification

The preparation of PCNs by in situ organomodification does not require pretreatment of the clay simplifying the procedure and reducing the production cost.

Kato et al. [65] and Alaoui et al [69] performed the cationic exchange using alkylammonium directly in the extruder. Kato et al [65] used a non standard extruder equipped with a long barrel (length: diameter 77:1) enabling for long residence time. They reported fine nanoscale dispersions. The final composites exhibited mechanical properties comparable to those of equivalent composites produced by conventional compounding. The in situ organomodification technique has been applied for the preparation of nanocomposites based on thermoplastic polymers such as PP, polystyrene (PS) [42,65,131,132] and PA6 [133,134]. XRD patterns confirm the in situ organomodification of the MMT by the ammonium salts and show that the greater shear leads to larger peaks at greater interlayer spacing for PP nanocomposites. TEM pictures show poor clay dispersion which was confirmed by mechanical testing. In the case of PA6/clay nanocomposites, the authors reported evidence of the nanocomposite structure by the TEM and XRD analyses but in which co-exist an intercalated and a delaminated structure [133,134]. However, the in situ organomodification does not solve the drawback of the thermal degradation of the quaternary ammonium salt by Hoffmann elimination.

1.3.3.2.2 Melt compounding without organomodification: water-assisted extrusion

In the last decade, significant effort has been devoted to the fabrication of polymer/untreated clay nanocomposites by melt compounding processes. Several authors have attempted to produce polymer/untreated clay nanocomposites by taking advantage of the natural affinities between water and untreated clay, using water as an in situ intercalating/exfoliating agent in

the extrusion compounding process. The literature on water-assisted extrusion processes for the fabrication of polymer/pristine clay nanocomposites becomes now rather abundant. Two main methods have been developed.

- **Direct water injection during extrusion**

The first publication concerning a well-exfoliated non hydro soluble polymer nanocomposites obtained by swelling MMT with water has been reported by DSM in a patent in 1999 [135]. This invention focuses on the preparation of PA6 nanocomposites with adding water. The mixing is carried out in a twin-screw extruder equipped with a water injection system and a degassing zone (Figure 1.3). The special design of the screw allows the pressure to increase up to 125 bar in this zone which prevents water evaporation. After being mixed with the PA6/pristine montmorillonite (p-MMT) mixture, water is removed further downstream via a venting gate before the composite exits from the extruder (Figure 1.3). Exfoliated PA/p-MMT nanocomposites were obtained using water injection without requiring the expensive clay organomodification. The patent claims the applicability of the technique to all polymers containing the polar amide (CONH) function between repeating aliphatic units. Since this pioneering work, different research groups reported the aid of water for the elaboration of nanocomposites based mainly on polar (PA) [64,66,67,72,73] but also on PP [65,69,75], styrene-acrylonitrile (SAN) [70,71], PET [78] and bio-based matrices (e.g. Nylon 11 (PA11)) [77], using p-MMT or o-MMT or other inorganic nanoparticles (e.g., HNTs, cellulose fibres) [30,31,68]. Delamination of p-MMT at the nanoscale was readily achieved in PA6 [64,66,67,72,73]. The figures 1.4 and 1.5 show TEM images of a PA6/ p-MMT composite with and without water injection. These micrographs prove that the injection of water in the system during extrusion greatly enhance the extent of exfoliation and dispersion of p-MMT in the PA6 matrix. The exfoliated morphology and the interface adhesion between clay and PA6 are explained by polar interactions. The proposed mechanism, which allows the dispersion and the exfoliation of the p-MMT into the matrix, is the following: (1) water acts as a swelling agent of the p-MMT and as a plasticizer of the nylon. It penetrates the clay layers and exfoliates them; (2) under the shear forces in the extruder, the exfoliated platelets are dispersed in the polymer matrix; (3) water is then evacuated from the extruder and the layers remain dispersed in the matrix due to the favourable interactions between polar MMT platelets and polar PA6.

Fedullo et al. [66,67] explained the process and the driving forces, which are leading to exfoliation/intercalation of the p-MMT in a PA6 matrix using the water injection extrusion process. A schematic description of the model used to explain exfoliation of p-MMT in PA is shown in Figure 1.6. Although this model is described step by step, in the extruder, everything happens simultaneously. Water is injected in the molten PA at high temperature and pressure and it plays two roles during extrusion processing:

(1) At the processing conditions of temperature and pressure water is miscible with the polyamide. It forms a one phase system of high polarity and lower viscosity. The demonstration of the miscibility of PA6 and water has been confirmed by using High Pressure Differential Scanning Calorimeter (HPDSC). A high pressure thermogram of neat PA6 and PA6 with the addition of 20% of water at 80 bar is presented in Figure 1.7. Neat PA6 exhibits a melting peak (T_m) at 220°C and, upon water addition, T_m shifts down to 157°C. This large cryoscopic effect witnesses a water PA miscibility as also observed by Vinken et al. [136], by Wevers et al. [137,138], by Bashek et al. [139] and more recently by Charlet et al. [140] and by Stoclet et al. [77] in the case of PA11. This phenomenon is observed for whatever the PA type and even for copolyether amide [74]. A more precise comprehensive study has shown that a fixed water concentration and a minimum applied pressure are required to achieve the PA6 dissolution [140]. An increase of pressure does not affect significantly the melting temperature; it has been shown that an increase in pressure of 100 bar (10 MPa) brings about a change in T_m of less than 2°C. Also, it has been shown that the conditions to obtain the maximum depression are a water concentration of 30 mass%.

(2) Then, water diffuses between the MMT layers and is adsorbed on the surface, resulting in a swelling of the clay and in the increasing of the interlayer distance.

These two effects allow PA chains to diffuse and adsorb onto MMT surface. When the PA chains diffuse into the interlayer space, they adsorb on the clay platelets and desorb water molecules, which are removed through atmospheric and vacuum degassing sections. The diffusion and the adsorption of PA6 chains on MMT have been shown thermodynamically favoured by Fermeglia et al. [126] and are explained by a variation of the internal energy. The adsorption of the PA chains is proven by the change in crystalline structure of the PA6 and by TGA and WAXS analysis on the extracted platelets.

Moreover, the water didn't seem to cause any decrease in the molecular weight of polyamide [135]. This is explained on the one hand, by the short contact time between polyamide melt and MMT platelets and on the other hand, by relatively low processing temperature in comparison with the polyamide melting temperature. Furthermore, the mechanical properties of neat PA with and without water injection are similar (see Table 1.1). This result support that the water addition doesn't cause detrimental PA's degradation by hydrolysis. In addition it appears that the PA6 miscibility with water greatly improves the dispersion of the clays into the matrix as shown by Touchaleaume et al. [73] in the case of PA6 /p-MMT nanocomposites and in the case of PA11/p-MMT by Stoclet et al. [77] (Figure 1.8). It has been shown that an exfoliated morphology can be obtained even for a clay content of 10%wt. The same conclusions have been reported for HNTs nanocomposites, which highlights the positive effect of injecting water during extrusion [26,30,31]. The nanocomposites obtained with this water injection system exhibit mechanical properties similar to the nanocomposites prepared with organoclay. For example, some mechanical properties of the PA6 nanocomposites are synthesized in Table 1.1 [64]. The yield strength and Young's modulus of the nanocomposite with water injection are better than those of both neat PA and PA/p-MMT without water injection. This improvement is directly related to the better dispersion of the layers in presence of water. Its Young modulus and yield strength are also enhanced of about 20% and 10% respectively compared to PA6/o-MMT. However, the toughness (notched impact stress) and the ductility (elongation at break) of polyamides/p-MMT extruded with water are lower than those of the neat polyamides. This effect can be explained by the formation of α -crystals or γ -crystals respectively in absence or in presence of water [64,77].

Table 1.1: Mechanical properties of the neat PA6, PA6/p-MMT composites obtained with and without water and PA6/o-MMT [64].

	Water (g/min)	Izod Impact Strength (J/m)	Young's modulus (GPa)	Yield Strength (MPa)	Elongation at Break (%)
PA6	0	84.5 $\pm$ 4.3	2.16 $\pm$ 0.11	71.1 $\pm$ 0.7	96 $\pm$ 18
	4.5	87.8 $\pm$ 2.2	2.21 $\pm$ 0.14	70.1 $\pm$ 0.4	129 $\pm$ 56
PA6/5wt% p-MMT	0	58.3 $\pm$ 6.5	2.55 $\pm$ 0.05	74.1 $\pm$ 0.7	25 $\pm$ 4
	4.5	52.9 $\pm$ 4.0	3.18 $\pm$ 0.05	81.7 $\pm$ $\pm$ 0.3	13 $\pm$ 2
	9	56.1 $\pm$ 8.1	3.32 $\pm$ 0.03	79.7 $\pm$ 0.9	16 $\pm$ 5
PA6/5wt% o-MMT	0	83.0 $\pm$ 6.9	2.77 $\pm$ 0.07	73.8 $\pm$ 1.1	24 $\pm$ 4

This route has been used by Stoclet et al. [77] to prepare a 100% green nanocomposite composed of the bio-based PA11 and p-MMT with high performances. Particularly at low shear rate and for a clay content of 10%wt, the Young's modulus can be doubled as compared with the unfilled polymer (Figure 1.9). The origin of this mechanical properties enhancement has been explained by a structural characterization. Indeed, the XRD study showed that there is a strong affinity between the polymer and the clay platelets confirmed by a change of the crystalline structure induced by the presence of the clays. At high shear rate, the effect is less obvious and is explained by an overheating which probably promotes polymer degradation. Nevertheless, this increase is noticeable and comparable to the one reported by Liu et al. in the case of well dispersed PA6/o-MMT nanocomposites [127] or for PA11/o-MMT nanocomposites [141].

This phenomenon is not likely to occur in the case of less polar matrices, explaining the limited success of this method with such matrices. For example, Rousseaux et al. [75] injected water in an extrusion stream composed of PP-g-MA and p-MMT but did not observe any enhancement in dispersion compared with conventional compounding. They attributed this result to a re-aggregation of the clay upon water removal, due to the high difference of polarity between p-MMT and PP-g-MA. In opposite, Lecouvet et al. [30] showed that water injection enables to improve considerably the clay dispersion.

As mentioned before, Kato et al. [65] and Alaoui et al. [69] performed the cationic exchange with alkyl ammonium salts directly in the extruder with injected water. However, although the authors show the feasibility of performing the cationic exchange directly in the extruder, their method does not eliminate the need for an organic modifier [65,69]. The method developed by Korbee et al. from DSM [135] was also applied to the production of polymer nanocomposites based on organophilic montmorillonite. Rousseaux et al. [75] showed that injection of water in a PP-g-MA stream enhanced the dispersion of methyl tallow bis-2-hydroxyethyl modified montmorillonite (Cloisite 30B) compared with conventional compounding. They attributed this result to the occurrence of an esterification reaction between the hydroxyl functions of the intercalating agent and the carboxyl functions of PP-g-MA. Again, while this result is interesting, it does not eliminate the need of an intercalating agent.

- **Slurry route**

In 2003, Hasegawa et al. [142] reported a compounding process for the preparation of PA6 nanocomposites, using p-MMT water slurry as an alternate for o-MMT. If the use of water is similar to the DSM patent, in this process, a suspension of p-MMT in water is injected within molten PA6 using an extruder, followed by removing the water as shown in Figure 1.10. TEM micrographs show that the mixture obtained with this clay slurry is exfoliated although a few silicate stacks are still visible. The XRD pattern shows that the formation of a slurry enhances the dispersion of the clay platelets in comparison with a dry compounded composite.

The mechanism of dispersion of the clay platelets in PA6 proposed by Hasegawa et al is explained on Figure 1.11. According to these authors, the exfoliation of silicate layers into the matrix occurs as follows: (1) the clay slurry is first pumped into the melting polyamide under vigorous shear (Figure 1.11a); (2) during blending, the slurry drops become smaller and the water begins to evaporate due to contact with melting PA (Figure 1.11b and c); (3) the vacuum bent evacuates the evaporated water. During evaporation, the platelets are dispersed into PA melt as monolayer or as a few layers (Figure 1.11d). Also, epoxy/clay have been successfully prepared by this route [92].

The proposed mechanism of dispersion of layered silicates in this process is quite different from the one of conventional compounding process using organophilic clay. When using organoclay, the polymer chains first intercalate into the stacked silicate galleries and then clay layers are exfoliated. In the slurry process, the silicate layers pre-exfoliated in water (slurry) are directly fed into the polymer matrix. No re-aggregation of the silicate layers is claimed. Some injection and compression molding experiments showed that the dispersion of the silicates platelets was stable. At small clay loading, the strength, modulus and heat distortion temperature of the nanocomposite were much higher than those of neat PA, but the impact strength was lower. Although the MMT layers are well dispersed in the matrix, the final properties of these nanocomposites are nearly equal to those of conventional PA6 o-MMT nanocomposites.

Unfortunately, the large water/clay ration, the very low throughput of 2 kg/h and the very high residence time of 10 min make this technique unsuitable for industrial applications. Recently, Stoeffler et al [76] have carried out a work which aims at comparing the efficiency of three melt compounding methods for preparing PA12/untreated clay composites. They confirm the potential of water-assisted extrusion processes to significantly enhance the dispersion state in

PA12/p-MMT composites. However, despite a drastic reduction in clay microparticles size, improvements in mechanical properties remained limited, due to the fact that clay remained mainly dispersed at the microscale. Therefore, they concluded that the use of water-assisted processes should be restricted to the preparation of composites based on untreated inorganic particles, devoted to applications for which the presence of an organic intercalating agent is highly undesirable.

1.4 Nanocomposite properties

Polymer layered silicates nanocomposites exhibit many advantages especially the exceptional improvements in properties at lower filler concentrations compared to conventional micro- and macro-composites [2]. Indeed, numerous studies have demonstrated that only a few percent of layered silicate can lead to a wide array of property enhancement, e.g. increased stiffness and strength, enhanced solvent and UV resistance, improved gas barrier properties and superior flame retardancy [1-3,12-14,26,30,31]. In this section, only the thermal properties are discussed.

1.4.1 Thermal Stability

The thermal stability of polymeric materials is usually studied by thermo-gravimetric analysis (TGA). Generally, higher thermal stability is commonly observed when clay platelets are well-dispersed into the polymer matrix, as a result of limited oxygen supply, hindered out-diffusion of the volatile decomposition products and also of char formation that acts as physical barrier between the polymer and the oxidative medium. In general, it has been reported that the PCNs are thermally more stable than pure polymers [1,2,4,12,23,28,75,77,146].

Moreover, despite the general improvement of thermal stability, decreases in the thermal stability of polymers upon nanocomposite formation have also been reported, and various mechanisms have been put forward to explain the results. It has been argued, for example, that after the early stages of thermal decomposition the stacked silicate layers could hold accumulated heat, acting as a heat source to accelerate the decomposition process, in conjunction with the heat flow supplied by the outside heat source [55]. Also, for polymers that require high melt processing temperatures, the thermal stability of the organic component of the modified clay, often alkyl ammonium cations could suffer from decomposition following the Hoffman elimination reaction. Indeed, the thermal degradation of organophilic

clays begins generally at 180°C [15,17,19,20,129]. During the melt compounding, surfactants moieties migrate outside of the silicate and influence the properties of the materials negatively [7]. Because of its degradation at low temperature, the organo-modifier catalyzes the thermal degradation of the polymer matrix [15-19], it plasticizes the polymer matrix [35-38], or diffuses out of the material, causing undesirable color, odor and taste to the composite [20]. As an alternative to the use of organomodified clays, recent studies have pointed out, as discussed earlier, the use of raw clay with the aid of water (an in situ intercalating/exfoliating processing aid).

By using this moulding process, Yu et al. [64], Dasari et al. [43] and Touchaleaume et al. [73] have shown that the PA/p-MMT with water assistance unlike PA/o-MMT presents a high thermal stability by TGA. Figure 1.12 shows the degradation onsets ($T_{-5\%}$) of PA6 nanocomposites and neat extruded PA6. The degradation temperature measured for the composite with water injection is higher than the one without water and the one of pure PA6 and polyamide-6/o-MMT nanocomposites. The PA6/p-MMT thermal stability improvement, achieved thanks to water injection, is ascribed to the better clay dispersion which acts as a barrier to the gas permeation. This barrier effect is reinforced through the formation of a protective inorganic layer [26,30-32]. Also, Touchaleaume et al. [73] have demonstrated in the case of PA6 that using water during melt compounding helps to prevent matrix degradation by decreasing the processing temperature due to the cryoscopic effect, which allows decreasing the extrusion temperature (down to 190°C) below the neat PA6 melting temperature (256°C), thus limiting the thermal degradation. The water also contributes to limiting the degradation because of its lubricating effect.

1.4.2 Flame retardancy

Because of the large use of polymers especially in domestic applications and in order to make them more safer, there is need to reduce their potential for ignition or burn. Traditionally, flame retardancy has been achieved either by using intrinsically flame retardant polymers (fluoropolymers or PVC), or by incorporating flame retardants (FRs) (such as aluminium trihydrate, magnesium hydroxide, organic brominated compounds) or intumescent systems. However, such FRs exhibit significant drawbacks. For example, aluminum trihydrate and magnesium hydroxide need to be applied at very high loadings to be effective. Use of halogenated additives is increasingly contested due to their potential toxicity related to the release of corrosive and toxic decomposition products such as halogen acids and metal halides

[147,148]. Considering also these disadvantages of traditional FRs, it becomes obvious that it is necessary to develop novel synergistic flame retardant systems with high efficiency and acceptable environmental impact. Therefore, recently, extensive research in the field of polymer nanocomposites have demonstrated that clay nanoparticles can contribute to the reduction of the flammability of polymeric materials and so could be a potential alternative to conventional flame retardants [26,30-32]. The three most widely used tests to measure the flame retardancy of polymeric materials are the cone calorimeter, the limiting oxygen index (LOI) and the UL-94 vertical burning test.

Cone calorimetry is one of the most effective medium-sized fire tests used to investigate the flame retardancy of polymeric materials under forced flaming conditions [149, 30-32]. This technique is based on the oxygen consumption principle with the assumption that there is a constant relationship between the mass of oxygen consumed from the air and the amount of heat release during the combustion of a material subjected to a given heat flux. The most important flammability parameters are: heat release (HRR), peak of heat release rate (pHRR), total heat release (THR), peak of mass loss rate (pMLR), time to ignition (TTI) and mass fraction of the residue.

Pioneering studies by Gilman et al. [150-152] have reported large reductions in flame spread and prolonged burning times of polymer-clay nanocomposites in cone calorimetry. For instance a decrease of 63% can be achieved with only 5wt.% of nanodispersed MMT in PA6 (Figure 1.13) [150]. Similarly, Bourbigot and coworkers have shown that the pHRR of poly(lactic acid) (PLA) is lowered by about 40% when adding 4wt.% layered silicates [153]. The main mode of action of the clay minerals as fire retardants is based on a physical mechanism, that is to say barrier effects arising from charring reaction and the accumulation of minerals at the sample surface, which reduces the heat and mass transfers between gas and condensed phases. The incorporation of a relatively low amount of nanoclay in a polymer matrix enables the formation of a protective ceramic char-inorganic layer at the sample surface during the combustion process [26,30,150].

This mechanism has been put forward in most studies reporting on the flame retardant properties of nanocomposites. Also, it is believed that the excess quaternary ammonium surfactants used to disperse the clays, also increase the probability of early ignition [26,30,150]. As discussed previously, using the original melt-compounding with water injection can overcome the organomodification and helps to form a well-dispersed nanoclay

morphology. This novel processing route enables also to enhance the fire retardancy. Indeed, for example, in the case of polymer-halloysite (HNTs) nanocomposites, Lecouvet et al. [26,30-31] showed for polypropylene/HNTs [30], polyethersulfone/HNTs [31] and for polyamide12/HNTs [20] prepared by water-assisted extrusion that these nanocomposites exhibit the lowest flammability due to the well-exfoliated structure and the formation of a strong and cohesive char acting as a barrier to heat and mass transfer [30]. The example of PP/HNTs is illustrated in figure 1.14.

1.5 Towards fully green composites?

Green composites are a specific class of biocomposites, where a bio-based polymer matrix is reinforced by natural fibers (cellulose, starch, lignin,...), and they represent an emerging area in polymer science. Increasing environmental awareness and lower material costs are the main driving forces for using renewable materials, such as wood and cellulose fibers, as reinforcement in polymer composites. A very appealing characteristic of natural fibers is also the fact that they can be considered as carbon dioxide neutral materials, i.e. they do not release excess carbon dioxide into the atmosphere when composted or combusted [144]. Other main advantages of natural fibers over the synthetic and inorganic fibers traditionally used as reinforcement in polymeric composites are low specific weight, high specific strength and stiffness, safer handling and working conditions and non-abrasiveness to the processing equipment [144]. When the used reinforcement is in nanoscale, such as nanocellulose, even further improvements in the composite properties can be obtained.

So far, research in the field of biocomposites has focused strongly on the materials used in the composite preparation, and not so much on the processing on the materials, even though the latter has a large impact on the final properties of the material. One of the most commonly used methods in the industrial processing of polymer composites is the extrusion process.

However, there are also some problems related to the use of natural fibers in thermoplastic composites. Major drawbacks are the poor interfacial adhesion between the hydrophobic matrix and the hydrophilic fibers and the difficult dispersion of fibers in the matrix. Because of the hydrophilic nature of natural fibers, they need to be dried before the compounding step. In addition, the processing temperatures are limited due to the thermal degradation of the natural organic fibres (mainly wood constituent) in temperatures above 200°C, hence limiting the range of suitable matrix polymers. Because of the low thermal stability of wood, only polymers with processing temperatures lower than 200°C are typically used in wood polymer

composites (WPCs). The polymers used are mostly low-cost commodity thermoplastics and the most common polymers used in WPCs are polyethylene (PE), polypropylene (PP) and polyvinylchloride (PVC). Despite this, any temperature overshoot, even localized, during the processing leads to an undesirable brownish discoloration often together with an unpleasant odor due to pyrolytic degradation of the cellulosic fibres [68]. This problem is getting worse with the increase of shear. Additives like coupling agents, light stabilizers, pigments, lubricants, fungicides and foaming agents are usually added to reduce this discoloration via reduced frictional degradation during compounding, but they are generally considered to be detrimental to adhesion [140,141] and then to mechanical properties. Soulestin and co-workers [68] investigated the possible extension to cellulosic nanofibres of an original process with water injection extrusion developed for nanoclays (described previously). Indeed, water is known to be efficient for removing organic components such as flavour volatiles, surfactant moieties by steam flushing during extrusion cooking processes [145]. When water is injected, the volatile moieties of the extrusion-degraded surfactant are steam stripped out of the processing media. The well-known flushing mechanism was reported for polyether-block-amide (PEBA)/o-MMT nanocomposites [20][74], and quantified thanks to odours and volatile organic compounds emissions analyses [20]. In the case of Low Density Polyethylene (LDPE)/cellulose fibers composites, Soulestin et al. have shown also that the injection of water during extrusion is really effective in improving dispersion of cellulose fibres and enables to achieve a complete disaggregation of cellulose clusters in addition to classical ways. Moreover, this technology allows to reducing significantly the yellowing of these composites, as can be seen in the figure 1.15. An odour stabilization has been also reported when water is used. Presence of water acts as a lubricant, plasticizer reducing the thermal degradation of the cellulose fibres during the severe processing conditions but without releasing significant amounts of nanofibres.

This work presents a clear indication that this novel processing route may be suggested to prepare polyolefins–biofibre composites. Also, with this technology offers the opportunity of technology transfer of nanocomposites “odour” solutions towards biocomposites based on natural fibres.

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Figure captions

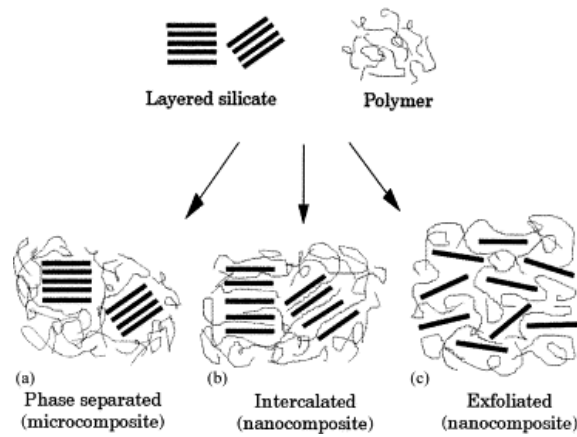


Figure 1.1: Scheme of different types of composite arising from the interaction of layered silicates and polymers: (a) phase-separated microcomposite; (b) intercalated nanocomposite; (c) exfoliated nanocomposite [1].

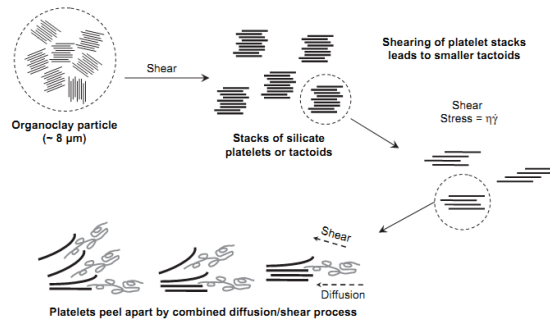


Figure 1.2: Mechanism of organoclay dispersion during melt compounding [44].

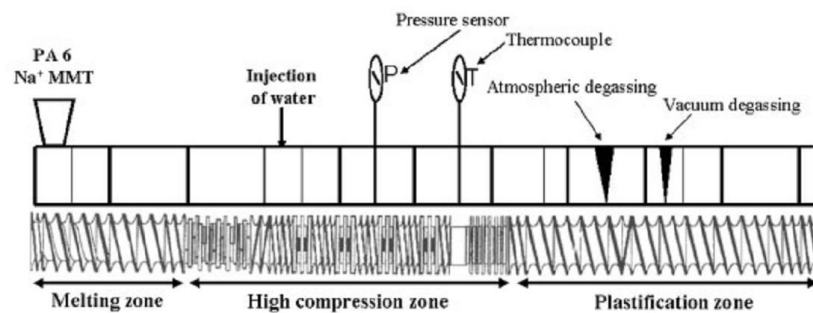


Figure 1.3: Screw configuration of the twin screw extruder used for the water-assisted preparation of the nylon 6/MMT nanocomposites [66].

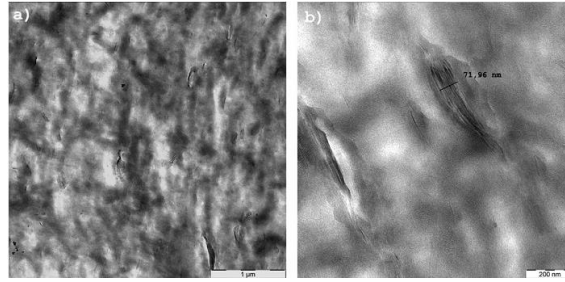
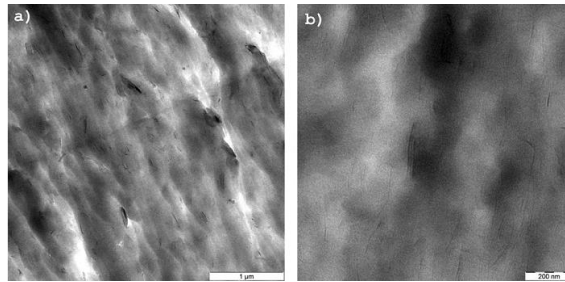


Figure 1.4: TEM micrograph of PA6/p-MMT (5wt.%) nanocomposites prepared by extrusion at 200rpm and without water injection (a) 5000x; (b) 16,000x [67].



Figures 1.5: TEM micrograph of PA6/p-MMT (5 wt.%) nanocomposites prepared by extrusion at 200rpm and with water injection (a) 5000x; (b) 16,000x [67].

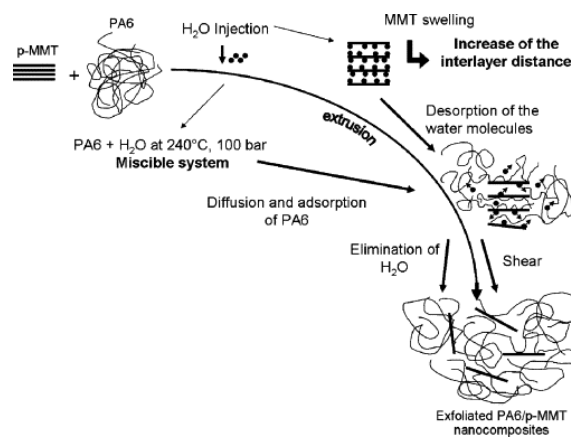


Figure 1.6: Schematic description of the dispersion of the p-MMT in a polyamide matrix during extrusion with the water injection system [67].

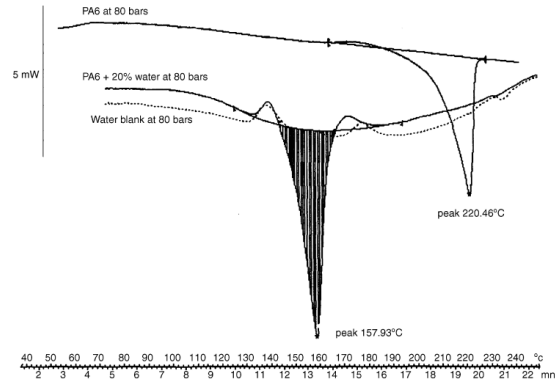


Figure 1.7: High pressure DSC thermogram of polyamide 6 with water. The dot line represents the thermogram of water at 80 bar [67].

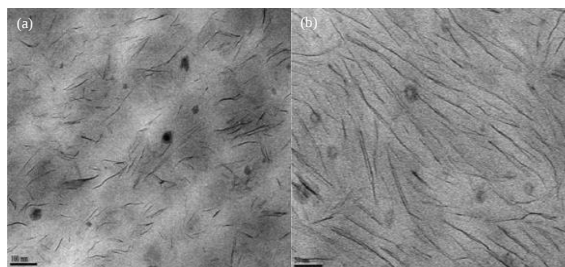


Figure 1.8: TEM observations of PA11 nanocomposites based on pristine clay filled at (a) 5%wt and (b) 10%wt. with water injection [77].

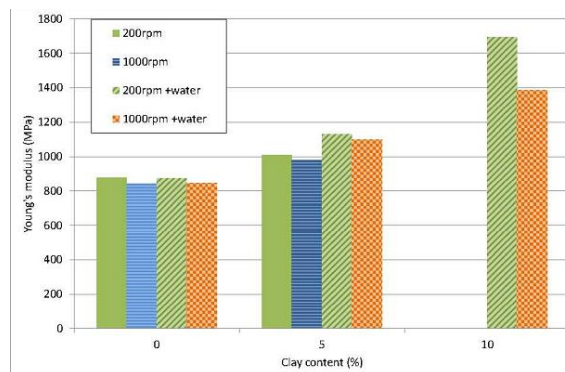


Figure 1.9: Evolution of Young's modulus as a function of clay conditions for PA11 nanocomposites elaborated under different conditions [77].

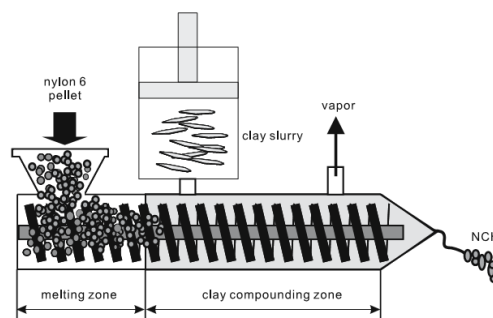


Figure 1.10: Schematic figure depicting the compounding process for preparing the Nylon6/Clay Hybrid - Clay Slurry using the clay slurry [142].

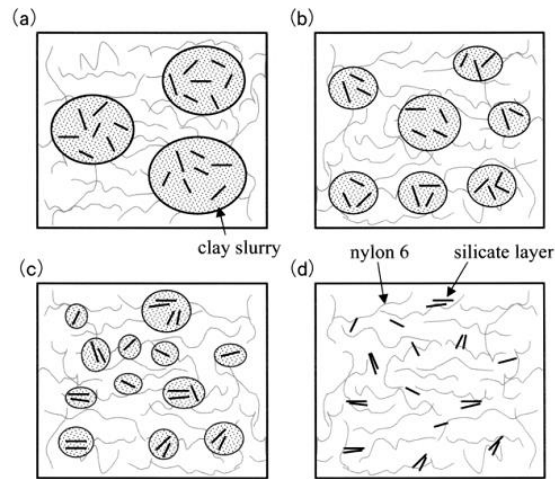


Figure 1.11: Schematic figure depicting the dispersion of the Na-montmorillonite silicate layers of the slurry into nylon 6 during compounding [142].

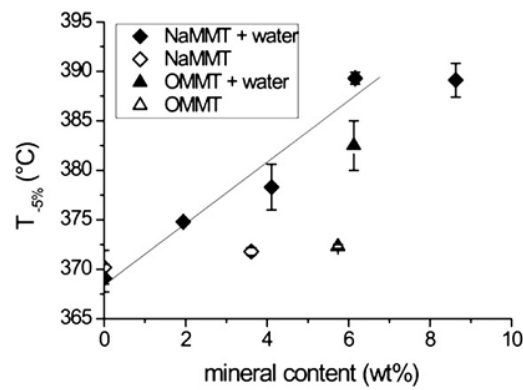


Figure 1.12: Onset of thermal degradation of PA6/clay nanocomposites [73].

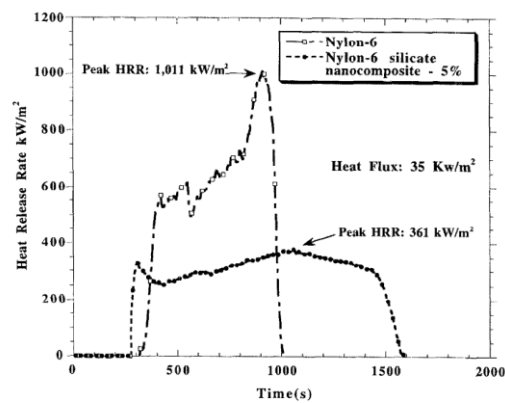


Figure 1.13: Comparison of the Heat Release Rate (HRR) plot for nylon-6 silicate- nanocomposite (mass fraction 5%) at 35kW/m² heat flux, showing a 63% reduction in HRR for the nanocomposite [150].

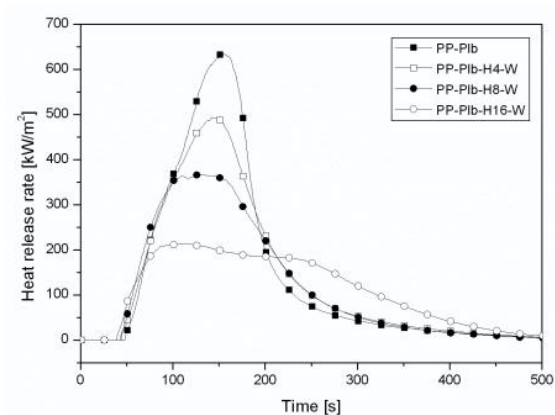


Figure 1.14: Heat release rate curves as a function of HNTs (H) loading for reference and PP/HNTs nanocomposites prepared by water-assisted extrusion (W) with PP-g-MA (Plb) [30].

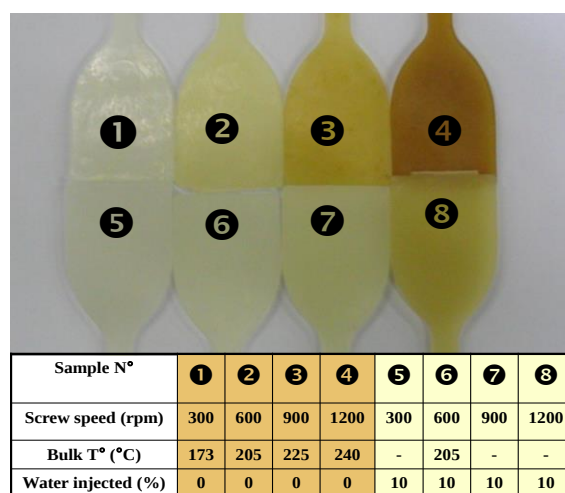


Figure 1.15: Picture of the LDPE/5% cellulose fibres composites produced without (sample 1 to 4) and with water injection (sample 5 to 8) with experimental parameters used for the preparation of the LDPE/cellulose composites.