



Université catholique de Louvain
Institute of Condensed Matter and Nanosciences (IMCN)
Molecules, Solids and Reactivity (MOST) &
Bio- and Soft Matter (BSMA)

Polypropylene/Clay Nanocomposites Revisited

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Thesis Advisors: Professor J. Marchand-Brynaert
& Professor P. Godard

Thesis submitted to obtain
the degree of Ph.D. in Science

Louvain-la-Neuve, 2010



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Louvain-la-Neuve, 2010

A ma fille, ma femme et mes parents.

Remerciements

“La passion pour la recherche”. C’est cette flamme qui m’a animé durant 4 ans, cette expérience tant humaine que professionnelle qui restera pour moi inoubliable et ce qui, aujourd’hui, me donne l’envie de vous la faire partager...

Je tiens tout d’abord à remercier de tout cœur mes promoteurs, le Professeur Jacqueline Marchand-Brynaert et le Professeur Pierre Godard, pour m’avoir donné l’opportunité de réaliser un travail de recherche dans ce domaine très passionnant des nanocomposites. Si j’ai pu mener à bien ce projet, c’est en grande partie grâce à leurs conseils avisés, leur générosité et leur soutien constant. Je tiens également à remercier le docteur Véronique Carlier pour avoir œuvré à la mise en place de ce projet de recherche.

Je remercie les membres de mon jury de thèse de s’être intéressés à ce travail, pour leur jugement pertinent sur mon manuscrit et pour le temps qu’ils y ont consacré.

J’exprime également toute ma reconnaissance à Michel Sclavons, pour sa disponibilité, son aide précieuse et surtout pour tous les bons moments passés durant ces années.

Je remercie par ailleurs le Fonds pour la formation à la Recherche dans l’Industrie et dans l’Agriculture (FRIA), dépendant du Fonds de

la Recherche Scientifique (FNRS), dont le soutien financier a permis la concrétisation de cette thèse.

Je tiens à exprimer toute ma gratitude envers mes collègues du laboratoire POLY. Merci pour ces années délirantes passées parmi vous. Je ne peux me retenir de faire un clin d'œil tout particulier à Guido, Xavier, Julian, Cédric, Anne-Christine, Vincent, Nicolas, Pascal, François, et Edwin.

La réalisation de ce travail multidisciplinaire a été rendue possible grâce à la collaboration des personnes qui m'ont encadré ou aidé dans les différents domaines abordés ; c'est pourquoi mes remerciements vont également à Xavier Drooghaag, Gaetan Henry, Pascale Lipnik, Pascal Van Velthem, Christophe Matthieu, Etienne Moniotte, Jonathan Van Leemput, Maria Taravella, Lionel Remy et Nicolas Mahy.

Un tout grand merci aussi à Chantal Delaet et Aurore Becquevort pour leur bonne humeur et pour l'attention qu'elles m'ont porté.

Merci infiniment à mes parents, qui m'ont toujours soutenu et qui m'ont permis d'entreprendre ces études dans des conditions idéales. J'adresse aussi un merci à toute ma famille et mes amis.

Un immense merci à ma femme Nathalie pour sa présence, sa patience, son soutien et ses encouragements de chaque instant. Je ne te remercierai jamais assez d'avoir été de tout cœur avec moi, particulièrement ces derniers mois.

Aurélie, merci pour tes beaux sourires qui ont été pour moi, source d'inspiration.

Merci enfin à tous ceux qui, de près ou de loin, m'ont aidé à la réalisation de cette thèse.

Avant-Propos

Cette thèse apporte un nouvel éclairage sur un procédé bien établi de fabrication des nanocomposites polypropylène (PP)/argile. Grâce à leurs propriétés thermiques, mécaniques et rhéologiques remarquables, ces matériaux se retrouvent dans de nombreuses applications industrielles (automobile, emballage, etc.). Cependant, des améliorations sont encore souhaitables, tant au niveau des coûts de production, qu'au niveau d'une optimisation, substantielle ou même modeste, des propriétés. La fabrication des nanocomposites PP/argile fait habituellement intervenir trois acteurs, à savoir le PP, un agent compatibilisant et une argile organomodifiée, via un procédé de mise en oeuvre par extrusion du mélange fondu ("melt-compounding"). En dehors du PP qui est le partenaire immuable, nous avons fait varier systématiquement les autres paramètres de la synthèse et étudié leur influence sur les propriétés des nanocomposites d'un point de vue fondamental. Le compatibilisant est un PP greffé à l'anhydride maléique (PP-g-MA), "fait maison" et répondant à un cahier des charges adapté à notre objectif. L'argile native, modifiée in situ par des carboxylates organiques peu coûteux, a remplacé les argiles organomodifiées classiques, thermiquement instables. Le procédé d'extrusion a été amélioré par l'injection d'eau dans la matière fondue. Nous avons combiné ces modifications validées individuelle-

ment, dans un procédé final innovant qui constitue une alternative très efficace par rapport à l'état de l'art actuel. Un effet de synergie entre les partenaires a été clairement mis en évidence. Nous invitons le lecteur à suivre cette aventure au travers d'un recueil de publications rassemblées sous l'intitulé "Polypropylene/Clay Nanocomposites revisited".

Abstract

This thesis is devoted to the optimization of polypropylene (PP)/clay nanocomposites preparation by trying to resolve or find alternatives to the actual limitations of producing PP/clay nanocomposites which restrain their industrial development.

A large part of this work is focused on the study and optimization of functionalized polypropylenes as compatibilizers. New PP ionomers based on elastomeric highly functionalized PPs-graft-maleic anhydride (PP-g-MAs) are investigated. Elastomeric highly functionalized PP-g-MAs are prepared by adding large amounts of N-bromosuccinimide (NBS) during the reactive extrusion process. They possess very high MA contents, high molar masses but exhibit no crystallinity and unfortunately, they are immiscible with PP and consequently cannot be used as compatibilizers in PP/clay nanocomposites. In view to optimize the PP-g-MAs synthesis for the preparation of model PP-g-MA/clay nanocomposites and PP/clay nanocomposites, new NBS-mediated PP-g-MAs were prepared by adapting the amount of NBS during the synthesis. The new NBS-mediated PP-g-MAs have significantly higher graft content than classic PP-g-MAs prepared without NBS while they keep acceptable molar masses and are miscible with PP. Used as compatibilizers, NBS-mediated PP-g-MAs clearly raise the clay dispersions and properties of PP-g-MA/clay nanocomposites in comparison to classic PP-g-MAs (i.e. prepared without NBS). An “optimized” NBS-mediated PP-g-MA sample was selected as compatibilizer and the resulting PP/clay nanocomposite shows much better clay dispersion and properties improvement than when

prepared using a classic PP-g-MA compatibilizer.

The synthesis and characterization of carboxylate clays was fully investigated in view to examine alternatives to alkylammonium clays for the preparation of PP/clay nanocomposites. Carboxylate clays which are synthesized from unmodified clay and anhydrous sodium acetate, are more thermally stable than a classic alkylammonium clay and do not degrade at extrusion temperature. The resulting PP-g-MA/carboxylate clay composites show better clay dispersion and properties enhancement than PP-g-MA/unmodified clay. The sodium acetate intercalated into the clay interlayer neutralizes the anhydride/acid functions of PP-g-MA during the compounding with the carboxylate clay. The best improvements of clay dispersion and properties enhancements were obtained when preparing nanocomposites from unmodified clay by synthesizing in situ the carboxylate clay and PP-g-MA ionomer with sodium acetate.

The elaboration of PP/(organo)clay nanocomposites was also investigated through a water-assisted extrusion process. The combined use of water injection and high-shear rates during the production of nanocomposites showed a remarkable synergy effect in increasing the organoclay exfoliation into a PP-g-MA matrix. An esterification reaction occurred between the hydroxyl functions of the organoclay surfactant and the carboxylic acids of PP-g-MA resulting from the anhydride hydrolysis. When producing PP-based nanocomposites, the best clay delamination degree and properties enhancement were reached by dilution into PP of PP-g-MA-based masterbatches synthesized with water injection and high-shear rates.

At last, the traditional elaboration of PP/clay nanocomposites was revisited by using the different knowledge developed in this work. PP/clay nanocomposites were processed through a one-step water-assisted extrusion method using optimized PP-g-MA compatibilizers, carboxylate salts and native clay. The in situ synthesis of carboxylate clay and PP-g-MA ionomer through sodium acetate addition and with the help of water injection was found to be an effective alternative to organoclay for the

elaboration of PP/clay nanocomposites. NBS-mediated PP-g-MA, and even more its ionomer, were found to be much more effective as compatibilizers than the classic PP-g-MA and its ionomer. Nevertheless, the highest level of clay delamination and best properties improvements were reached when combining the use of NBS-mediated PP-g-MA, sodium acetate, water injection and organoclay. The examined properties were the thermal properties (by thermogravimetric analysis), the mechanical properties (by tensile tests) and the rheological properties (by plane-plane rheology).

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Abbreviations

η^* complex viscosity

AFM atomic force microscopy

C30B Cloisite 30B, organoclay

CNa Cloisite Na, untreated clay

cND corrected neutralization degree

DSC differential scanning calorimetry

E' Young's modulus

elPP-g-MA elastomeric polypropylene-graft-maleic anhydride

equiv. equivalent

FTIR Fourier transform infrared spectroscopy

G' elastic modulus

GPC gel permeation chromatography

HDPE high-density polyethylene

HTM hexadecyl trimethylammonium

IC inorganic content

LDPE low-density polyethylene

LLDPE linear low-density polyethylene

MA maleic anhydride

MAO methylaluminoxane

MB masterbatch

MeOH methanol

MMT montmorillonite

NaAc sodium acetate

NaBut sodium butyrate

NaMMT sodium montmorillonite

NaOH sodium hydroxide

NaPro sodium propionate

NBS *N*-bromosuccinimide

NC nanocomposite

ND neutralization degree

NF948 Nanofil 948, organoclay

NMR nuclear magnetic resonance

NVP *N*-vinylpyrrolidone

ODA octadecyl acrylate

OMMT organomodified montmorillonite, organoclay, alkylammonium
Montmorillonite

OP one-pot process

OTM octadecyl trimethylammonium

PA	polyamide
PCNs	polymer/clay nanocomposites
PDMS	polydimethylsiloxane
PE	polyethylene
PEO or PEG	poly(ethylene oxide), poly(ethylene glycol)
Plb	Polybond 3200, commercial PP-g-MA
PMMA	poly(methyl methacrylate)
PMMT	alkylphosphonium Montmorillonite
PO	polyolefin
PP	polypropylene
PP-g-MA	polypropylene-graft-maleic anhydride
PP-t-NH ₃ ⁺	ammonium-terminated polypropylene
SAN	poly(styrene-co-acrylonitrile)
SAXS	small angle X-ray scattering
SP	sequential process
SS	screw speed
TCB	1,2,4 trichlorobenzene
TEM	transmission electron microscopy
T _g	glass transition
TGA	thermogravimetric analysis
TP	throughput
TPEs	thermoplastic elastomers

W water injection rate

WAXS wide angle X-ray scattering

XRD X-ray diffraction

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Chapter 1

A Review on Polymer/Untreated Clay Nanocomposites

A Review on Polymer/Untreated Clay Nanocomposites

Dimitri D.J. Rousseaux, et al.

Selected sections from a complete review article to be submitted.

1.1 Introduction

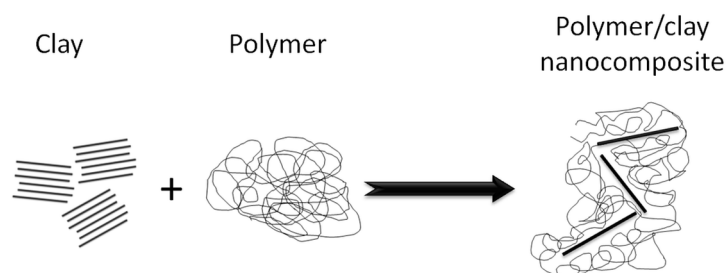


Figure 1.1: Illustration of the structure of polymer/clay nanocomposite.

Polymer/clay nanocomposites (PCNs) are polymers reinforced with clay particles, mainly phyllosilicates, having at least one dimension in the nanometer scale (Figure 1.1). During the last decades, PCNs received a considerable scientific and technological attention mainly due to their unique combination of properties. A few percents 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 filler, the reinforcement efficiency of the composite can be significantly better than with conventional mineral fillers [5]. As an example, Figure 1.2 shows that 5 wt.% of well-dispersed MMT into TPO matrix has the same reinforcement effect on the modulus than 25 wt.% of talc.

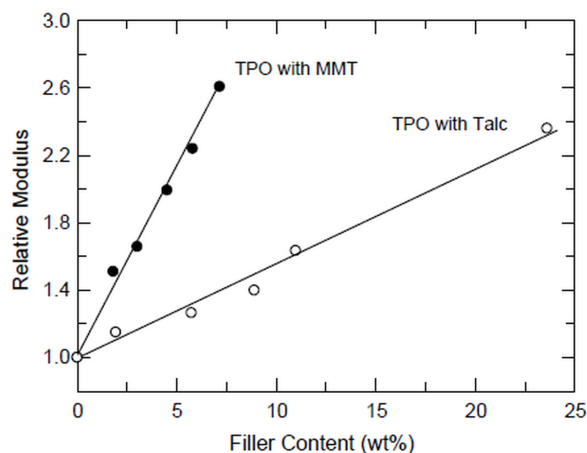


Figure 1.2: Comparison of relative modulus as a function of filler content of thermoplastic polyolefin (TPO) composites formed from melt mixing with Montmorillonite (MMT) and with talc. [From Lee et al.]

PCNs technology originated in the late 1980's at Toyota's Central R&D laboratories [6]. Toyota, studying mainly nylon composites, holds the basic patents on their production [7–10]. Nowadays, several books [11–13] and reviews [1, 2, 14, 15] treat on PCNs. The present work briefly recalls the different existing ways to produce PNCs from clay and polyolefins, focusing more deeply on unmodified clay.

Montmorillonite (MMT) is the most employed clay for the preparation of PCNs. MMT is a natural layered aluminosilicate mineral, member of the smectite family. It is a 2:1 clay, one clay platelet consisting of two SiO_4 tetrahedral sheets sandwiching a central $\text{Al}(\text{O},\text{OH})_6$ octahedral sheet (Figure 1.3). In smectites, trivalent aluminium cations of the octahedral layers are partially substituted by divalent magnesium cations. The overall negative charge of the clay is balanced by hydrated counter-cations (sodium, calcium) in the interlayer. In sodium Montmorillonite (NaMMT), there are only sodium cations in the interlayer. (Na)MMT silicate layers present a high aspect ratio (length/thickness ratio) with

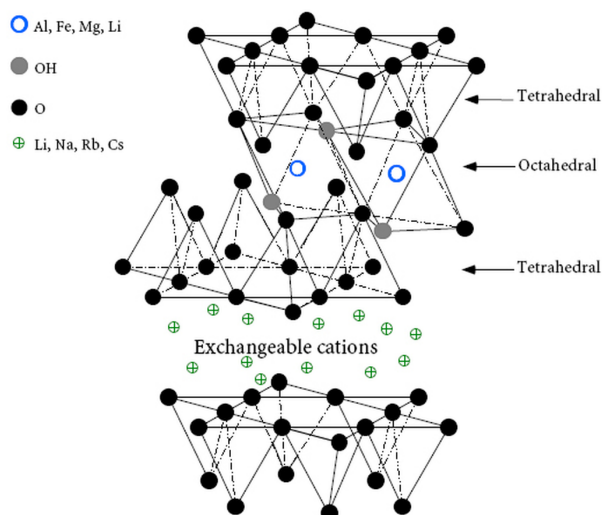


Figure 1.3: Structure of 2:1 layered silicate [from Giannelis et al.]

their one nanometer thickness and hundreds nanometers length. They offer thus a large surface area for polymer/filler interactions.

MMT layers are naturally stacked into aggregates of several microns and need to be separated and dispersed into the polymer matrix to obtain a nanocomposite (Figure 1.1). Depending on the nature of the clay and polymer matrix and the method of preparation, three main types of structure can be observed: phase separated microcomposite, intercalated nanocomposite and exfoliated nanocomposite (Figure 1.4). The more separated and dispersed the clay layers are, the higher the surface area for polymer/filler interactions and the better the overall properties enhancement.

Polyethylene (PE) and polypropylene (PP) are indubitably the most widely used polyolefin (PO) polymers (Figure 1.5). As they have huge academic and industrial importance, it is not surprising that they have attracted great interest in the nanocomposites emerging field. However PO/clay nanocomposites are significantly more difficult to obtain than

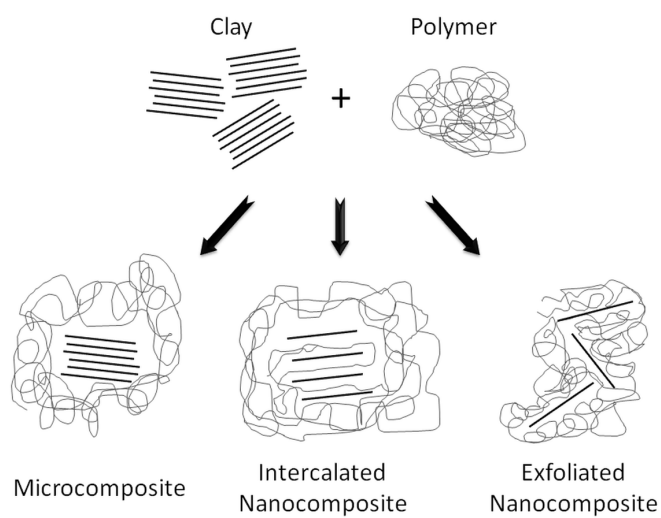


Figure 1.4: Scheme of different types of composite arising from the interaction of layered silicates and polymers.

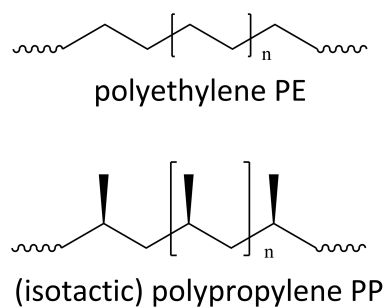


Figure 1.5: Polyethylene and isotactic polypropylene structure.

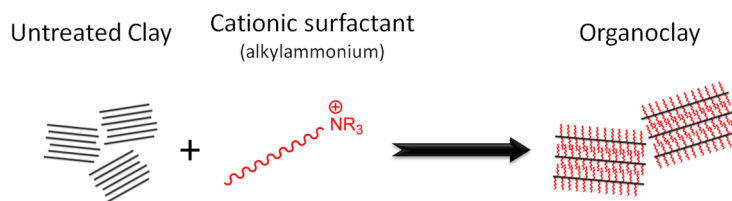


Figure 1.6: Illustration of the structure of organoclay.

that from polar matrix like polyamides. As they do not include any polar group on their backbone, polyolefins are not compatible with untreated silicate layers. Moreover, the dispersion of clay into a polymer requires sufficiently favorable enthalpic contributions to overcome the entropic unfavorable ones resulting from the confinement of the polymer chains inside the gallery of the silicate layers [16, 17]. Polyolefin-based PCNs researches are therefore almost exclusively focused on the use of chemically modified layered silicates. Organomodified Montmorillonite (OMMT) ion-exchanged by alkyl ammonium ions are generally employed (Figure 1.6).

Nevertheless with apolar matrix the use of organomodified-clay is not sufficient to obtain nanocomposites due the great difference of polarity with the polyolefin. The use of a compatibilizer including polar functions is required, in addition of the organoclay, to obtain good interfacial interaction between the polyolefin and the layered silicate. The choice of the polymeric compatibilizer is critical for optimizing the properties of polyolefin clay nanocomposites. The compatibilizers allow interactions with the oxygen atoms on the clay surface and must be miscible with the bulk polyolefin. Generally polyolefin grafted maleic anhydride are used as compatibilizers (Figure 1.7).

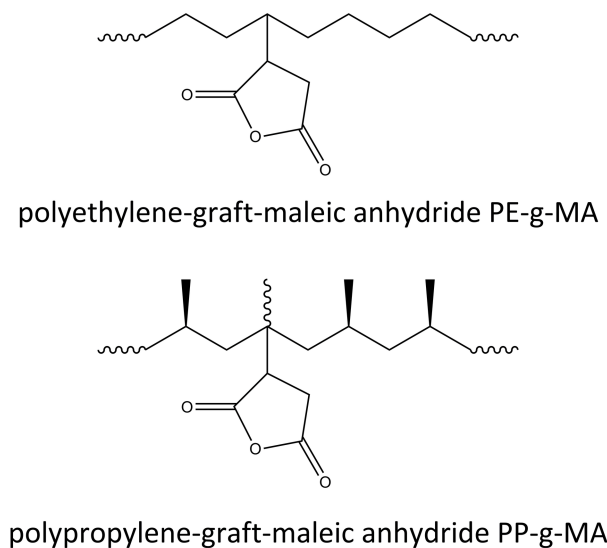


Figure 1.7: Structure of polyethylene- and polypropylene-graft-maleic anhydride.

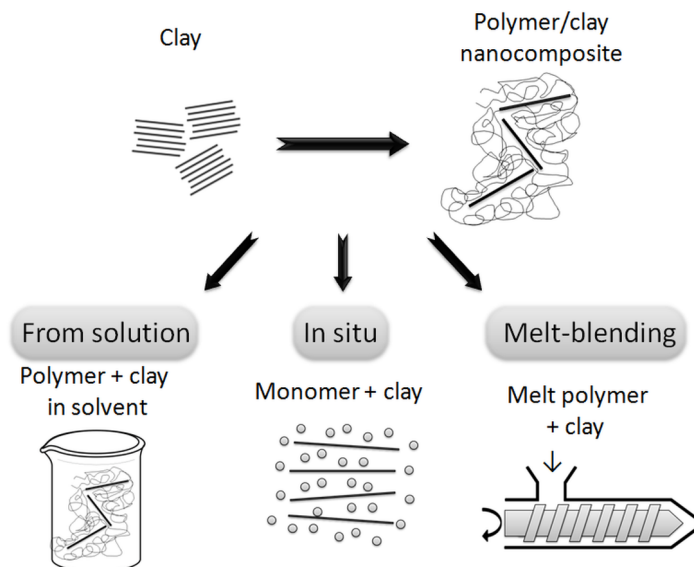


Figure 1.8: Scheme of the main ways to synthesize polymer/clay nanocomposites.

1.2 Nanocomposites from organoclay

Three different preparative methods exist to synthesize polyolefin/clay nanocomposites using organoclay (Figure 1.8): intercalation of the polymer from solution, *in situ* intercalative polymerization and melt intercalation.

1.2.1 Intercalation from solution

Aromatic solvents such as xylene or toluene are generally used to dissolve polyolefins. As aromatic solvents are apolar, the use of organoclay is required to allow the organoclay swelling into the solvent. If it is not sufficient, a more polar co-solvent like benzonitrile can be used. Very few literature reports were found on polyolefins nanocomposites obtained by this method.

Jeon et al. [18] reported intercalated high-density polyethylene (HDPE) nanocomposites obtained by solution blending of HDPE with 20 wt.% of OMMT (NaMMT intercalated by dodecylammonium) in a co-solvent of xylene and benzonitrile followed by precipitation in THF. XRD results show that intercalation of OMMT by HDPE was achieved but TEM pictures reveal fairly large clay stacks indicating poor clay dispersion.

Song et al. [19] obtained exfoliated HDPE nanocomposites using a solvothermal preparation: HDPE is first swelled in toluene into a sealed tank at 170 °C for 1 h and cooled to room temperature. A solution of OMMT (NaMMT intercalated by hexadecyl trimethylammonium) dispersed in toluene is added into the tank and the mixture is heated at 170 °C for 2 h followed by toluene evaporation. The exfoliated structure of PE/OMMT nanocomposites was confirmed by XRD and TEM analyses; a clay separation of 10 nm or more was observed.

Chiu et al. [20] studied solution mixed PP/OMMT nanocomposites without compatibilizers. PP and 5 wt.% of OMMT (NaMMT intercalated by hydrogenated-tallow dimethylammonium or methyl tallow

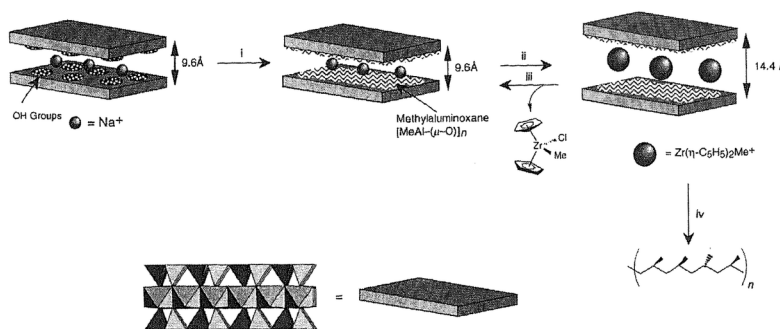


Figure 1.9: Schematic representation of the modification and ion-exchange of the clay with zirconocene catalyst followed by propene polymerization. [From Tudor et al.] i, MAO, toluene, 24 h room temp.; ii, $[\text{Zr}(\eta\text{-C}_5\text{H}_5)_2\text{Me}(\text{THF})]\text{BPh}_4$, MeCN, 12 h, room temp.; iii, NaCl, THF, 12 h, room temp.; iv, propylene, 5 bar, 45 °C, toluene

bis-2-hydroxyethylammonium) are dissolved in 1,2,4 trichlorobenzene (TCB), cast onto stainless dishes and TCB is evaporated. As nano-scaled dispersion is visible by TEM, the authors conclude that compatibilizers are not required to develop solution-mixed PP/OMMT nanocomposites. The thermal stability of PP/OMMT nanocomposites was enhanced regarding pure PP.

1.2.2 *In situ* intercalative polymerization

An appropriate catalyst is needed to polymerize the olefin between the clay layers. Ziegler-Natta catalysts can be used but generally metallocene catalysts are employed because there are more tunable.

Tudor et al. [21] were the first to use this method to produce PP/clay nanocomposites using a zirconocene catalyst ($[\text{Zr}(\eta\text{-C}_5\text{H}_5)_2\text{Me}(\text{THF})]^+$) and methylaluminoxane (MAO). MAO removes acidic protons, increases the interlayer spacing and allows the metallocene catalyst to be inserted (Figure 1.9). When the catalyst is added, a cation exchange reaction occurs between Na^+ from the clay (smectite Laponite) and the metallocene catalyst. The resulting intercalated materials were shown re-

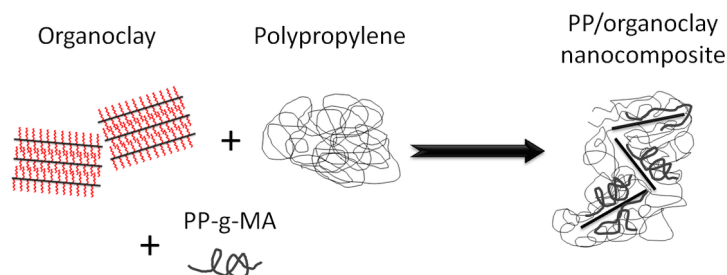


Figure 1.10: Synthesis of polypropylene/organoclay nanocomposites.

markably active catalysts for propylene polymerization. Unfortunately, the authors did not characterize the composites.

Heinemann et al. [22] obtained HDPE and LLDPE/organoclay nanocomposites by ethene homo- and copolymerization (with 1-octene) using a MAO-activated zirconocene, nickel and palladium catalysts in the presence of organoclay (sodium bentonite intercalated by dioctadecyl dimethylammonium). While Tudor et al. [21] introduced MAO and then the catalyst into the clay before polymerization, here the clay is dispersed into toluene, the dispersion is saturated with ethene and the polymerization is started by adding the catalysts and MAO solution. TEM pictures show the coexistence of an intercalated structure and an exfoliated structure.

He et al. [23] produced exfoliated PP/alkyl-triphenylphosphonium-modified montmorillonite (PMMT) nanocomposites by *in situ* intercalative polymerization of propene with a clay-intercalated Ziegler-Natta $\text{TiCl}_4/\text{MgCl}_2/\text{PMMT}$ catalyst. The synthesized PP possesses high isotacticity, melting point and molar masses. TEM pictures confirm the exfoliated structure of the PP/PMMT nanocomposites. TGA measurements also show an improved thermal stability of the PP/PMMT nanocomposites regarding the PP synthesized in absence of PMMT.

1.2.3 Melt intercalation

Melt compounding is the most common way to produce polyolefin/clay nanocomposites and this process is mainly described in literature. The melt-mixing of the three components, i.e. PP, compatibilizer (usually a PP-g-MA) and organoclay, is the most practical way to prepare polyolefin/clay nanocomposites (Figure 1.10).

Okada's team [24–26] firstly reported the elaboration of PP/organoclay nanocomposites by melt blending using PP grafted with maleic anhydride (PP-g-MA) oligomers as matrix and as compatibilizers. Two important parameters have been determined: the intercalation capability of the compatibilizer in the silicate layers and the miscibility of the compatibilizer in the PP. Polar groups (maleic anhydride (MA) functions) are required to allow the clay layers to be intercalated by the compatibilizer but this may decrease the PP miscibility if the compatibilizer contains too many MA groups. The authors thus recommend to use PP-g-MA with larger miscibility to PP in order to improve the dispersibility of the clay. The authors also examined the effect of the PP-g-MA/clay weight ratio on the intercalation and showed a raise of the intercalation while increasing the PP-g-MA amount.

1.3 Nanocomposites from untreated clay by melt compounding process

The main disadvantage to use organomodified clays is the thermal decomposition of organophilic surfactant (usually a quaternary alkylammonium) which begins generally at 180 °C [27]. The extrusion temperature for PP is generally in the range of 200–250 °C, but the temperature in the melt at the output of the extruder can be higher than 300 °C due to the high shear. The surfactant degradation (mainly by Hofmann elimination) limits the clay dispersion and consequently the composite properties [28–31]. Moreover, surfactant decomposition products impart undesirable color, odor and taste to the composite [32].

Efforts have been made to synthesize more thermally stable organoclays using other cationic surfactants. For example pyridinium and quinolinium [33], imidazolium [34], phosphonium [35] and stibonium [36] 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.

The present review has the intention to treat the synthesis of polyolefin nanocomposites from untreated clay (generally sodium Montmorillonite, NaMMT). Very few literature reports exist. Polyolefin nanocomposites from untreated clay are almost exclusively synthesized by melt compounding. Some nanocomposites are produced from untreated clay using or not an *in situ* organomodification by quaternary ammonium-like surfactants or oligomers during the processing.

1.3.1 *In situ* organomodification

Wang and Wilkie [37] were the first to report the preparation of polypropylene and polystyrene nanocomposites by *in situ* reactive blending. The nanocomposites were produced by melt compounding, using different mixers and a twin screw extruder, of previously dry-mixed PP, NaMMT, ammonium salt, in the presence or absence of maleic anhydride (MA). PP nanocomposites from OMMT (NaMMT intercalated by dimethyl hydrogenated-tallow benzylammonium) with and without MA were also produced. The authors examined the effect of the particular organomodification of the clay, the effect of the maleic anhydride and the effect of shear on the formation of PP nanocomposites. XRD patterns confirm the *in situ* organomodification of the NaMMT by the ammonium salts and show that the greater shear leads to larger peaks at greater interlayer spacing. The addition of MA has a lesser important effect on the nanocomposite formation for PP than for PS. TEM pictures show poor clay dispersion and mechanical testing confirms the poor clay dispersion in PP. However a significant reduction in the peak heat release rate is observed in cone calorimetry suggesting that nano-

composites formation has occurred.

Tang et al. [38] used the *in situ* organomodification of NaMMT to produce PP nanocomposites by melt intercalation. They adapted to PP the “one-pot” method described by Alexandre and Dubois [39] to produce ethylene-vinyl acetate/clay nanocomposites. The nanocomposites were prepared on a two-roll mill by adding NaMMT and a quaternary ammonium salt (hexadecyl trimethylammonium bromide, HTM) to the molten PP. For comparison, they prepared a nanocomposite by adding an organoclay (OMMT). The authors reported evidences of a nanocomposite structure by TEM and XRD analyses in the case of NaMMT and HTM, while there is no visible intercalation of the polymer between the silicate layers for the composite prepared with OMMT.

The following papers deal about PP nanocomposites using *in situ* organomodification and PP-g-MA. Indeed, PP-g-MA is required in order to intercalate and disperse organomodified clays in the PP matrix [25].

The same team, Tang et al. [40], produced in another work PP nanocomposites using PP-g-MA in addition to PP, NaMMT and HTM by the same process. Processing shear influence was investigated (by using a twin-screw extruder or a Twin-roll mill). The authors provided a mechanism explaining the intercalation process of the untreated clay. The ammonium salt (HTM) diffuses into the clay interlayer and makes the NaMMT organophilic. At the same time, some free surfactant remains non-intercalated in the matrix (PP or PP+PP-g-MA) enhancing the compatibility during the polymer matrix intercalation into the clay interlayer. According to the authors, there is an interaction between the polymer matrix and the surfactant, like the interaction between the surfactant and the silicate. PP-g-MA may also intercalate NaMMT modified by HTM, increasing the compatibility when the polymer intercalates into the interlayer. Intercalation of PP matrix begins with the help of shear force when the “packing density” in the interlayer is sufficient, leading to an exfoliated or intercalated structure.

Kato et al. [41] developed a production method for PP nanocompo-

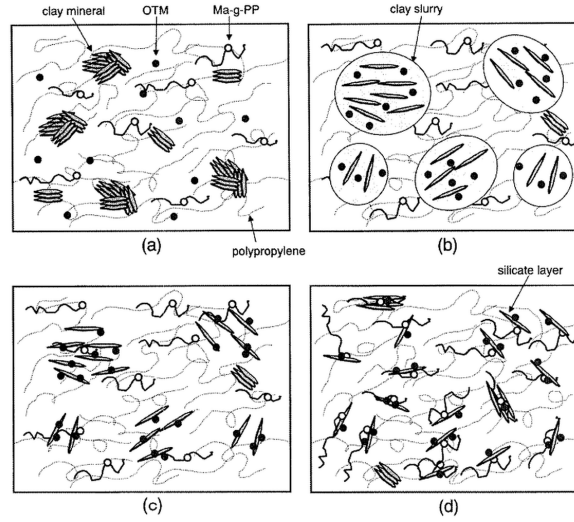


Figure 1.11: Schematic view depicting the dispersion of silicate layers of the clay in the PP during compounding by the extruder [From Kato et al.]

sites based on *in situ* organomodification of NaMMT by a quaternary ammonium salt (octadecyltrimethylammonium, OTM), a commercial PP-g-MA and water. A twin-screw co-rotating intermeshing extruder with a long screw (length-to-diameter ratio $L/D = 77:1$) at four geometrical sections was used to produce the nanocomposites. A premix of PP with NaMMT, OTM and PP-g-MA is melted in the first kneading section. Water is injected into the extruder in the second section. Multiple kneading screw elements are present in the second section to disperse the slurry of MMT silicate layers into PP. The following (third and fourth) sections include open and vacuum vent in order to remove the water vapor from the sample. For comparison, the authors prepared a conventional sample with OMMT (NaMMT intercalated by OTM). The mechanical properties of the sample made from NaMMT, OTM and PP-g-MA were almost the same as those of the conventional sample made from OMMT. According to the authors, in the conventional

method, the polymer chains intercalate into the galleries of the stacked layered silicates allowing the exfoliation into PP matrix, while following their method, the exfoliated silicate layers in water are directly fixed into the polymer matrix preventing any further aggregation. The authors considered that the dispersion mechanism of NaMMT into PP, depicted in Figure 1.11, as follows: after the dispersion of clay into PP (a), water swells the clay to form a clay slurry (b); the silicate layers from the slurry are dispersed in the PP under a strong shear and at the same time, a cation exchange occurs between the OTM and sodium cations of the clay (c); PP-g-MA helps to disperse NaMMT stabilized by OTM and when water is evaporated, the silicate layers are fixed (d). The preparation of PCNs by *in situ* organomodification does not require pretreatment of the clay simplifying the procedure and reducing the production cost. However, the *in situ* organomodification does not solve the drawback of the thermal degradation of the quaternary ammonium salt by Hofmann elimination.

1.3.2 Various ways without organomodification

Several approaches have been explored to produce PP clay nanocomposites from untreated clay without requiring (*in situ*) organomodification by a quaternary alkylammonium salt. The first route deals with ammonium-terminated PP (PP-t-NH₃⁺). The second approach involves the use of dispersants/intercalants/ exfoliants which are polymeric surfactants or copolymers that can directly intercalate untreated clay. The latter includes the use of poly(ethylene oxide), PEO-based surfactants or acrylate-based amphiphilic copolymers.

Wang et al. [42] reported exfoliated PP/clay nanocomposites using end-chain-functionalized PP-t-NH₃⁺, obtained by metallocene synthesis, as organic modification for montmorillonite. The authors prepared PP-t-NH₃⁺/NaMMT and PP-t-NH₃⁺/OMMT (NaMMT intercalated by dioctadecyl dimethylammonium) nanocomposites by static melt intercalation (static annealing in absence of shear or solvent). As both

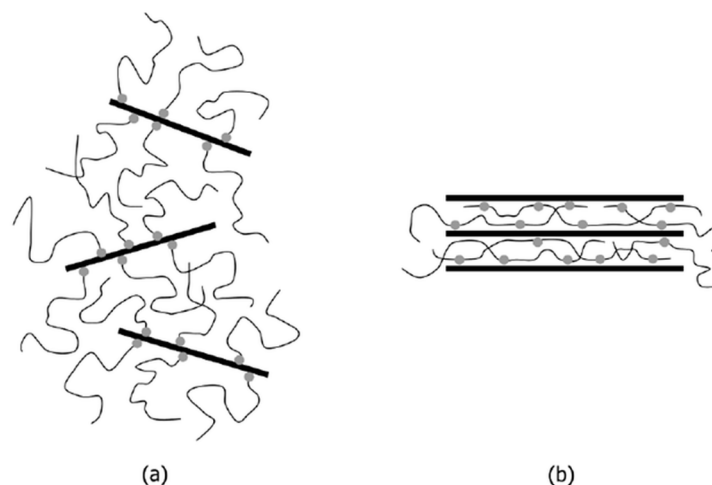


Figure 1.12: Illustration of the molecular structure of (a) chain-end-functionalized polyolefin and (b) side-chain-functionalized polyolefin located between clay interlayers

nanocomposites were exfoliated (no peak on XRD pattern), an organic surfactant is not required to promote compatibility between PP-t-NH_3^+ and NaMMT. Moreover, the nanocomposites were achieved in absence of shear; thus the dispersion is thermodynamically favored. The binary PP-t-NH_3^+ /NaMMT nanocomposite was subsequently mixed with neat PP and it was shown, by TEM and XRD, that the exfoliated structure is maintained. PP chains have served as diluents of the thermodynamically stable binary PP-t-NH_3^+ /NaMMT exfoliated structure. The authors also used side-chain-functionalized polyolefins to examine their ability to disperse OMMT. XRD patterns showed intercalated structure for all the binary side-chain-functionalized polyolefin/OMMT samples. Figure 1.12 illustrates the structural conformations of end-chain-functionalized and side-chain-functionalized polyolefins. End-chain-functionalized PP-t-NH_3^+ anchors the clay surface with the terminal hydrophilic NH_3^+ functions and exfoliates the clay platelets with the hydrophobic high

molar mass and semicrystalline PP chains. In contrast, side-chain-functionalized polyolefin forms multiple contacts with each of the clay surfaces, bridging consecutive clay platelets.

The same team, Xu et al. [43], studied further the rheological properties of layered silicates nanocomposites made from PP-g-MA and OMMT and compared them with nanocomposites made from PP-t-NH₃⁺ and NaMMT. Commercial PP-g-MA/OMMT and metallocene PP-t-NH₃⁺/NaMMT masterbatches were diluted into PP to achieve a composition of 67/28/5 weight percent (wt.%) of PP/PP-g-MA/OMMT and of 50/45/5 wt.% of PP/PP-t-NH₃⁺/NaMMT, respectively. Based on XRD and TEM investigations, the authors surmise that the nanocomposite based on the PP-g-MA/OMMT masterbatch displays well-dispersed (exfoliated) clay platelets, as well as tactoids containing multiple clay layers. For the nanocomposite based on the PP-t-NH₃⁺/NaMMT concentrate, no clay basal reflexion is observed in the XRD and TEM pictures indicate disordered tactoids morphology. In spite of the highly dispersed state of silicate layers and the expectation of a filler-network dominated response, the nanocomposite based on PP-t-NH₃⁺ exhibits liquid-like rheological behavior. The authors suggest that PP-t-NH₃⁺, which provides sufficient thermodynamic driving force for the dispersion of the clay, is unable to sustain a polymer mediated filler network structure. In contrast, the nanocomposite based on PP-g-MA exhibits solid-like rheological behavior which is consistent with the notion of a percolative filler network structure. Even if the clay dispersion is better with single-end functionalized ammonium PP, the more-than-one interaction sites per polymer chain in PP-g-MA allow for long-lived bridging interactions between the clay layers or their tactoids and therefore, a percolated structure. The authors believe that the main mechanism responsible for the changes in the viscoelastic behavior of such nanocomposites operates through a polymer mediated filler network and not necessarily through direct particle-particle interactions although the latter might become the dominant mechanism at high clay loadings.

The Manias' team works [42, 43] on the use of PP-t-NH₃⁺ as organic modification for NaMMT were promising. PP-t-NH₃⁺ intercalates untreated clay and improves clay dispersion in the PP nanocomposites in comparison with the classical PP/PP-g-MA/OMMT system. However, the authors conclude that PP-t-NH₃⁺ is unable to stabilize the dispersed silicate layers which requires more than one interaction sites per polymer chains.

The following papers deal with the PEO-based surfactant approach to produce PP clay nanocomposites from untreated clay.

Liao et al. [44] reported especially the use of PE-PEO diblock copolymers blended with NaMMT as fillers for the reinforcement of PE. NaMMT is first melt blended in an internal mixer with the PE-PEO diblock copolymer at 135 °C. The nanocomposites are prepared by blending PE and PE-PEO/NaMMT with a two-roll blender at 140 °C. Tensile tests show higher tensile strength of PE/PE-PEO/NaMMT nanocomposites than for the corresponding PE/NaMMT nanocomposites. This implies, according to the authors, that PE-PEO/NaMMT has good compatibility with PE. Unfortunately, neither XRD measurements nor TEM pictures were performed on the samples.

Fischer [45] reported in a symposium proceeding the use of PEO block copolymers to produce polymer clay nanocomposites from untreated clay. The PEO block acts as complexing group for the inter-layer sodium cations of the clay, hence ion-exchange reaction is not necessary (Figure 1.13). According to Fischer, the use of block copolymers as “macro-surfactant” compatibilizers is rather general; especially HDPE, LDPE, LLDPE and PP nanocomposites were successfully prepared. However, Fischer does not present any detailed result, except a SEM picture of a PP nanocomposite showing homogeneously distributed clays sheets.

Moad et al. [46] used PEO-based nonionic surfactants as dispersants/intercalants/exfoliants to prepare PP/clay nanocomposites from untreated montmorillonite clay (NaMMT). Various copolymers were ex-

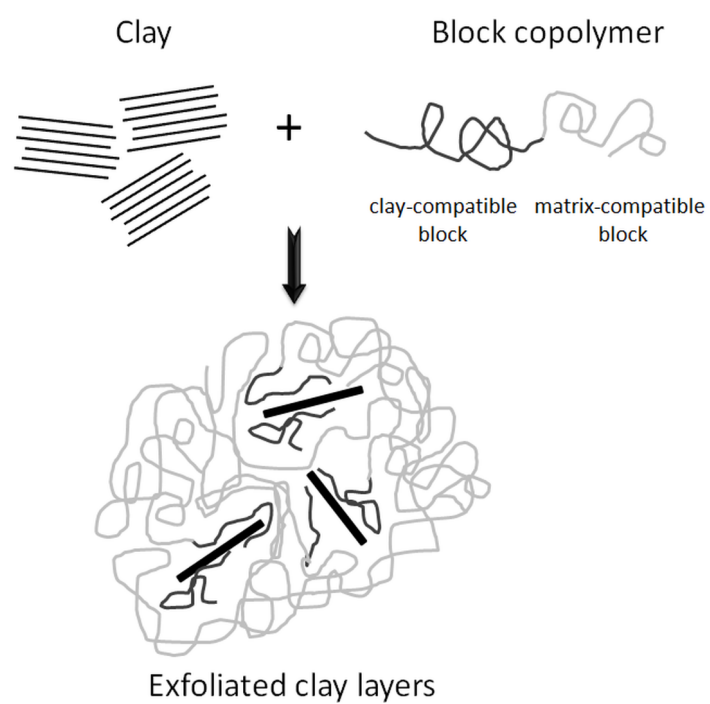


Figure 1.13: Schematic picture of the action of block copolymer for an exfoliation of clay sheets within a polymeric matrix

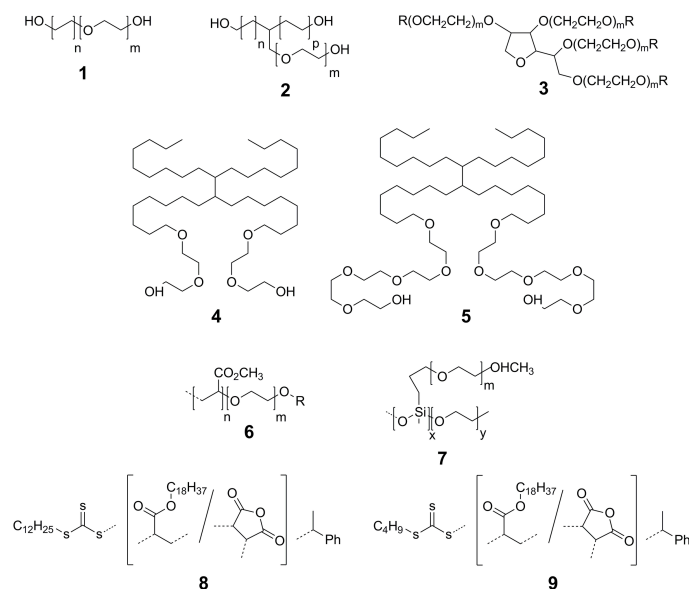


Figure 1.14: Surfactants examined by Moad et al.

plored (Figure 1.14): PE-block-PEO with linear PE chains (1) branched structures (2), sorbitan derivatives (3), gemini surfactants (4, 5), PMMA-block-PEO (6) and PEO-graft-PDMS (7). The nanocomposites were prepared by diluting a masterbatch of clay (10-25 wt.%) and surfactants into stabilized PP. Surfactants with longer PEO blocks expand more the layered structure. The higher clay expansion is obtained for PP/NaMMT nanocomposites with PMMA-block-PEO (6) and PEO-graft-PDMS (7) surfactants. The NaMMT expansion with PEO depends also on the PEO/clay ratio. Low levels of PEO expand the NaMMT of 0.4 nm which is attributed to the presence of a single layer of PEO. An expansion of 0.8 nm is observed at higher levels of PEO and is attributed to a double layer of PEO or possibly to a PEO helix. The authors observed however that there is no obvious correlation between the extent of exfoliation and the ability of the surfactant to expand the NaMMT structure. While large clay aggregates are observed by TEM for the PP/NaMMT composite without additive, the agglomerates are

largely broken down into tactoids of 3 to 10 clay layers with all the non-ionic surfactants. All the surfactants provide significant property improvements depending on the amount and the structure of the additive. PE-block-PEO copolymers with linear PE and short PEO blocks provided the best mechanical reinforcement. This leads the authors to conclude that substantial clay expansion is not necessary for exfoliation. Branched PE-block-PEO surfactants which have short PEO blocks provided more ductile nanocomposites than the linear surfactants. The optimal surfactant level was in the range of 1 to 3 wt.% with respect to PP, for 5 wt.% NaMMT/PP nanocomposite. Tensile and impact properties were significantly improved with 5 wt.% of NaMMT. The thermal and thermo-oxidative stability of the nanocomposites were also significantly better.

In a following paper, Moad et al. [47] summarized their previous work [46] and reported the use of two classes of dispersants (Figure 1.14): polyethylene oxide based non-ionic (PEO-block-PE) surfactants (1-5) and amphiphilic copolymers of long chain (meth)acrylates such as octadecyl acrylate [poly(ODA)] with a more polar co-monomer such as maleic anhydride [poly(ODA-grad-MA)] (8) or N-vinylpyrrolidone [poly(ODA-grad-NVP)] (9). The PE-block-PEO copolymer with linear PE and short PEO block (1) is especially compared to the amphiphilic copolymers (8) and (9). The nanocomposites are produced by dilution of a masterbatch of clay and surfactant in stabilized PP as in the previous paper. A reference nanocomposite is synthesized by using 5 wt.% of organoclay (Cloisite 20A) and 7.5 wt.% of PP-g-MA (Polybond 3200, 1 wt.% of MA). Both the non-ionic PEO surfactants and the acrylic copolymers provide only a small expansion of the clay ($d < 2$ nm). The PP/NaMMT nanocomposites with a PEO-based copolymer or with amphiphilic copolymers show significant improvements of their modulus (20-30 %) and are significantly more ductile than the reference PP/OMMT nanocomposite. Thermal (under nitrogen) and thermo-oxidative (under air) analyses show a significantly improved stability

for 5 wt.% NaMMT and 1 wt.% copolymer, with respect to PP or PP with NaMMT only. The improvement is more important with the acrylic copolymers than with the PEO-based surfactant, even if their thermo-oxidative stability is not as great as the reference PP/organoclay nanocomposite. According to the authors, the composite properties are not particularly dependent on the dispersant architecture (statistical, gradient or block copolymer) but strongly on the level of dispersant and its overall composition.

The Liao's [44], Fischer's [45] and Moad's [46, 47] works on the use of PEO-based surfactants and acrylate-based amphiphilic copolymers as dispersants/intercalants/exfoliants allow the production of polyolefin nanocomposites from untreated clay. Significant improvements in thermal and mechanical properties can be reached with 5 wt.% of clay and only 1 wt.% of dispersant.

1.3.3 Miscellaneous

Villaluenga et al. [48] studied gas transport properties of PP/clay composites membranes with NaMMT or OMMT. As no compatibilizer is used, no evidence of intercalation was found by XRD, the two samples being conventional microcomposites. Tensile properties show poor reinforcing effect of NaMMT, but are slightly better with OMMT. Thermal decomposition measurements are in both cases raised of about 20 °C. Appreciable reduction of gas permeability has been reached in both cases. This last effect is attributed to the tortuous path for diffusing gas molecules and reduced molecular mobility of polymer chains due to the presence of filler particles.

Recently, Perrin-Sarazin et al. [49] investigated the potential of ball milling to reach clay exfoliation in PP clay nanocomposites. Different formulations and conditions were studied. NaMMT and OMMT were ball milled alone or with other components (PP and/or PP-g-MA). The ball milled formulations were melt-compounded in a microextruder. Some formulations were directly melt-compounded after milling, others

were diluted in PP to maintain the same final clay content of 5 wt.% for both NaMMT and OMMT. As the OMMT contains 40 wt.% of surfactant, the inorganic clay content is rather 3 wt.%. Milling of clay alone leads to particle agglomeration and the resulting material shows poor clay dispersion. Less particle agglomeration is obtained with NaMMT than with OMMT. The presence of other components (PP and PP-g-MA) during the ball milling prevents only NaMMT to agglomerate. The ball milling was shown improving the clay dispersion especially with untreated clay.

1.4 Conclusions

Polyolefin/clay nanocomposites, despite extensive researches during the last decades, still show limited properties improvement, which restrains their industrial development. The main problem concerns the thermal stability of the alkylammonium surfactant in the organoclay when producing polymer/clay nanocomposites through melt-blending. Alkylammoniums usually decompose at extrusion temperatures leading to a collapse of the silicate layers and limiting the composite properties. Many alternatives to alkylammonium have been explored. The solutions proposing to start from untreated clay and to achieve the organomodification *in situ* were practical but do not resolve the thermal degradation drawback of the alkylammonium salts by Hofmann elimination. The idea to use ammonium-terminated polypropylene as organic modification for the untreated clay was bright. However, despite their ability to exfoliate the untreated clay, these materials are unable to stabilize the dispersed silicate layers. The use of PEO-based surfactants as “dispersants”, although providing significant thermal and mechanical improvements, is also expensive and/or requires multistep synthesis limiting large-scale production.

Nowadays, there is no real alternative (thermally stable and inexpensive alternative) of using the alkylammonium organoclays when syn-

thesizing polyolefin/clay nanocomposites. Our thesis aims at providing a novel insight into this old problem.

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Chapter 2

Objective & Strategy

2.1 Context of the thesis

This thesis has been realized in collaboration between two research poles of the Institute of Condensed Matter and Nanosciences (IMCN) of the Université catholique de Louvain (UCL): the entity “Organic and medicinal chemistry” (CHOM) of the pole “Molecules, Solids and Reactivity” (MOST) and the entity “Polymer sciences” (POLY) of the pole “Bio- and Soft Matter” (BSMA). The research was supported by the Foundation for Training in Industrial and Agricultural Research (FRIA) which depends on the National Foundation for Scientific Research (FNRS).

2.2 Preceding knowledge

In 2000, the POLY entity, linked to an European project “Melt Made Polymer nanocomposites (Meltanocomp)” [1], started a project which aimed at decreasing costs of the nanocomposites technology. This project allowed to develop in POLY, polyamide (PA)/untreated clay nanocomposites by avoiding the organotreatment to make the clay organophilic. The project was based on a water-assisted extrusion process in which PA and untreated clay are extruded while water is injected under pressure directly into the melt blend [2, 3].

The work on clay-based nanocomposites at POLY has been focused, up to now, on PA matrix and on the preparation of PA/clay masterbatches and their incorporation into polypropylene (PP). An original process, developed in POLY, recommends to use polypropylene-graft-maleic anhydride (PP-g-MA) as compatibilizer to react with end-chain amine groups of PA [4].

Since '90s, the grafting and characterization of polyolefins, especially PP-g-MA, have been extensively studied at POLY [5–8]. A new method to synthesize highly functionalized polyolefins has been developed in the frame of a project funded by the Walloon Region [9]. It is now possible to synthesize PP-g-MA with very high levels of anhydride grafting (2.5-

3 wt.%) without recovering grafted PP waxes [10].

The CHOM entity was more recently involved to this research for the preparation of model molecules of polypropylene (propene oligomer) and the understanding of the mechanisms involved in the reactive processing methods [11, 12].

2.3 Objective of the thesis

Despite extensive researches during the last decades, polypropylene/clay nanocomposites still show limited properties improvement (thermal, mechanical and rheological properties), even using organoclay and compatibilizers, which clearly restrains their industrial development. As pointed out in the first chapter, one of the main reason of the limited properties improvement is the poor thermal stability of the alkylammonium-surfactants in the organoclay. Many studies focused on this problem (see paragraph 1.3) but until now, there is no other real alternative to the one of using alkylammonium organoclays when producing polyolefin/clay nanocomposites. Indeed, the proposed solutions (other cationic surfactants; *in situ* organomodification; ammonium-terminated polypropylene; polyethylene oxide dispersants) are expensive and/or require multistep synthesis limiting large-scale production.

Another main reason of the limited properties improvement is that usual commercial PP-g-MAs have low MA content which restricts consequently the interactions between the clay and the compatibilizers. Contrary to the alkylammoniums thermal stability problem, almost no studies have examined this latter problem.

Another reason of the limited properties improvement is that the mechanisms of the clay dispersion into polyolefin matrices (intercalation and exfoliation) are currently not well understood making difficult to optimize the preparation of these nanocomposites.

In this context, the objective of this thesis is the optimization of polypropylene/clay nanocomposites preparation. This work aims at re-

solving or finding alternatives to the actual limitations of producing PP/clay nanocomposites which restrain their industrial development.

2.4 Scientific strategy and thesis map

In order to resolve or to find alternatives to the above mentioned limitations, several ways have been investigated.

A large part of this thesis is devoted to the study and the optimization of functionalized PP as compatibilizer. The chapter 3 focuses on the synthesis and characterization of PP ionomers based on highly functionalized PP-g-MA described by Henry et al [10]. The influence of the base nature and base amount on the neutralization degree and consequently on the material properties is investigated. A method to quantify the effective neutralization degree of the PP-g-MA ionomers is developed. The chapter 4 aims to optimize the PP-g-MA synthesis for the preparation of model PP-g-MA/clay nanocomposites and PP/clay nanocomposites. The challenge here is to increase the compatibility between PP-g-MA and clay in order to increase the clay dispersion while avoiding immiscibility between the PP matrix and the PP-g-MA compatibilizer. As producing polyolefin/clay nanocomposites from unmodified clay is a challenge, an “holy grail” in the nanocomposite field, both unmodified clay and organoclay have been used to help us during the investigations.

In the chapter 5, carboxylate clays are considered as an alternative to alkylammonium clays for the preparation of PP/clay nanocomposites. The synthesis and characterization of these carboxylate clays is fully investigated. These carboxylate clays are used to prepare and characterize model PP-g-MA/clay nanocomposites. A key feature is that the carboxylate salt which is intercalated between the clay layers, can partially neutralize the PP-g-MA into an ionomer. Nanocomposites were also prepared from unmodified clay by synthesizing *in situ* the carboxylate clay and PP-g-MA ionomer.

The chapter 6 discusses the preparation of PP/clay nanocomposites

by the previously mentioned water-assisted extrusion process. The first part of the work is a comprehensive study on the possible interactions occurring between clay and PP-g-MA with and without the help of water and/or high-shear rates. The second part is focused on the production and characterization of PP-based nanocomposites by dilution of PP-g-MA-based masterbatches into neat PP. To examine the relevance of the masterbatch dilution process, PP-based nanocomposites were also produced by an one-pot process in which PP, PP-g-MA and clay are directly melt-compounded together.

The chapter 7 is a conclusive and federalist work where PP/clay nanocomposites are prepared using the different knowledges developed in the preceding chapters. PP/clay nanocomposites are processed through water-assisted extrusion using optimized PP-g-MA compatibilizers, carboxylate salts and native or organomodified clays.

At last, we conclude on the novelties brought in this thesis and perspectives for future researches based on our work (Chapter 8).

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Chapter 3

Highly Functionalized PP-g-MA & Ionomer

Le premier acteur que nous avons étudié est le compatibilisant. Sur base du knowhow du laboratoire POLY, nous avons considéré des PP-g-MAs hautement greffés pour en faire des ionomères potentiellement utiles à notre projet. Ces nouveaux ionomères de PP-g-MAs hautement greffés possèdent des propriétés thermiques et rhéologiques intéressantes. Le procédé de fabrication des ionomères, impliquant de l'acétate de sodium hydraté, sera utilisé par la suite sur des PP-g-MAs optimisés pour l'élaboration de nanocomposites PP/argile.

Polypropylene Ionic Thermoplastic Elastomers: Synthesis and Properties

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Polym. Degrad. Stab. 2010, 95(3), p. 363-368.

Work presented at the 5th Biannual Conference on Modification, Degradation and Stability of Polymers (Modest), 2008 (Liège, Belgium).

Abstract

Polypropylene ionic thermoplastic elastomers have been prepared by melt radical grafting of maleic anhydride onto polypropylene in the presence of N-bromosuccinimide followed by neutralization of the resulting elastomeric grafted polypropylene using sodium salts. Sodium hydroxide and sodium acetate were compared in aqueous solution, as anhydrous or hydrated powders. The neutralization reaction was followed by Fourier transform infrared spectroscopy, allowing the development of a method to determine the effective neutralization degree. Important physical changes were recorded upon neutralization. Especially thermal stability, shear storage modulus and complex viscosity in the flow region were largely increased as a function of the neutralization degree.

3.1 Introduction

Ionomers are macromolecules composed of a small but significant proportion of constitutional units (less than 10 %) containing an ionic and/or ionizable group [1]. The ionic moieties are usually obtained by full or partial neutralization of the acid groups by metal salts. The acid groups are mainly carboxylic acids but also sulfonic and phosphonic acids are being used. The ionic groups cause a micro-phase separation

of the ionic moieties (ionic aggregation) within the non-ionic matrix and act as physical crosslinks [2–7]. The ionic aggregation induces strong modifications in the physical, mechanical and rheological properties of the material. Nevertheless, ionomers can be melt-processed due to the reversibility of the crosslinking based on the increased mobility of the ionic moieties at high temperature.

Ionomers of low glass-transition non-crystalline polymers can be used as ionic thermoplastic elastomers (TPEs) if the ionic aggregates are sufficiently weakened at the processing temperatures [8, 9]. TPEs are melt-processable polymers composed of a continuous elastomeric phase reinforced by a dispersed hard phase acting as thermo-reversible junction points [10].

Different types of carboxylated ionic TPEs have been studied in the past, for example: Kutsumizu et al. investigated non-crystalline poly(ethylene-co-methacrylic acid) ionomers [11, 12]; more recently, the group of Goossens-van Duin studied extensively ionomers based on maleated ethylene/propylene copolymers [9, 13–16].

In this paper, carboxylated ionic TPEs of polypropylene (PP) will be introduced. PP elastomeric ionomers are based on the elastomeric polypropylene-graft-maleic anhydride (elPP-g-MA) described by Henry et al. [17]. Both the precursor elPP-g-MA and the ionomers are synthesized by melt-processing. The neutralization reaction is monitored by infrared spectroscopy and a method is proposed to determine the effective neutralization degree (ND). Various forms of sodium hydroxide and sodium acetate are used to compare their efficiency for elPP-g-MA neutralization. The influence of the base nature and amount on the ND is studied. Thermal and rheological properties of the ionomers are examined and discussed as a function of the ND.

3.2 Experimental Section

3.2.1 Materials

Isotactic homopolymer PP powder (Moplen HF500N) was purchased by Basell. The free radical initiator was Luperox 101XLS50 from Arkema (2,5-bis(tert-butyl-peroxy)-2,5-dimethylhexane (DHBP), 50 wt% blend with silica). Maleic anhydride (MA, Acros, 99 % purity), N-bromosuccinimide (NBS, Acros, 99 % purity), sodium acetate (NaAc) trihydrate (Aldrich, 99 % purity) and anhydrous (Aldrich, 99 % purity), sodium hydroxide (NaOH) in pellets (Aldrich, 99+ % purity) and in powder (Aldrich, 97 % purity) and toluene (Fisher, analytical grade) were used as received.

3.2.2 Synthesis

elPP-g-MA synthesis. elPP-g-MA was synthesized by reactive extrusion as described by Henry [17]. Briefly, isotactic polypropylene was treated with 3.26 wt% of supported peroxide, 5 wt% of maleic anhydride and 0.8 wt% of N-bromosuccinimide¹. elPP-g-MA was produced in a Brabender single screw extruder equipped with a screw of L/D = 20. The barrel was heated at three zones at 220, 240 and 260 °C, respectively, and the screw speed was set to 30 rpm.

Ionomer synthesis. All the ionomers were synthesized by reactive blending in a Brabender Plasticorder equipped with an electrically heated W50EH mixing device of 40 g capacity. The mixing speed was set to 100 rpm and the temperature at 220 °C. The alkaline base was added to the molten elPP-g-MA either in fine powder, or in 2.5 molar aqueous solution, and the reaction was stopped after 5 min by quenching the molten ionomer at room temperature.

¹The assumed mechanism of maleic anhydride grafting onto polypropylene in the presence of N-bromosuccinimide is presented in the Appendix to Chapter 3

3.2.3 Characterizations

Quantification of the grafted species. elPP-g-MA samples were first washed as described in a previous paper [17]. Then, the anhydride content was determined by acid-base titration according to a standard procedure [18]².

Differential scanning calorimetry (DSC). Crystallinity and glass transition temperature (T_g) measurements of elPP-g-MA and ionomers were evaluated on a second heating ramp from -50 to 220 °C at 10 °C/min using a Mettler Toledo DSC 821e module. The device was calibrated with indium and zinc.

Size exclusion chromatography (SEC). Number- and weight-average molar mass (M_n and M_w , respectively) of the elPP-g-MA were measured on a Waters Alliance GPCV 2000 equipped with two Styragel HT 6E and one Styragel HT 2 columns. A differential refractometer and a viscometer were used as detectors. The mobile phase was 1,2,4-trichlorobenzene (TCB). The concentration of the sample was 2 mg/mL in TCB and dissolution was achieved by shaking at 160 °C for 1 h. The injection volume was 215 μ L. Temperature was held constant at 145 °C throughout the analysis. The system was calibrated prior to the analysis with PS standards according to ISO 16,014-2 specification.

Fourier Transform Infrared (FTIR) spectroscopy. FTIR spectra of compression molded films were recorded on a Nicolet Nexus 670 FTIR apparatus, over a spectral range from 4000 to 400 cm^{-1} at a resolution of 4 cm^{-1} . All the FTIR spectra were normalized by setting the peak height of the 973 cm^{-1} absorption band to an absorbance of 1 A.U. This band, which is assigned to isotactic helices, is usually considered as an internal reference for the comparison of films of different thickness [19]. The FTIR spectra were mathematically analyzed by an iterative curve-fitting method developed in the Igor software provided by Wavemetrics, Inc. The absorption bands area in the carbonyl frequency

²The procedure for the quantification of the grafted species is fully described in section 4.2.3. of Chapter 4.

Table 3.1: Characteristics of PP and elPP-g-MA

	PP	elPP-g-MA
Grafting level (wt%MA)	/	3.5
Crystallinity (%)	46.2	1.6
Mn	65k	22k
Mw	245k	60k

range of the anhydride ($1750 - 1830 \text{ cm}^{-1}$) and of the carboxylic acid ($1650 - 1750 \text{ cm}^{-1}$) were approximated by a Voigt function.

Thermogravimetric analysis (TGA). Thermal analyses were performed on Mettler Toledo TGA/SDTA 851e using a heating rate of $10 \text{ }^{\circ}\text{C}/\text{min}$ under air atmosphere ($100 \text{ ml}/\text{min}$) from 25 to $600 \text{ }^{\circ}\text{C}$.

Rheological properties. Rheological properties were measured using a Rubber Process Analyser RPA 2000 from Alpha Technologies. Frequency sweep tests were performed at $120 \text{ }^{\circ}\text{C}$ and at a strain rate of 10% over an angular frequency ranging from 300 to $1 \text{ rad}/\text{s}$.

3.3 Results and discussion

3.3.1 elPP-g-MA characterizations

Characterizations of PP and elPP-g-MA are summarized in Table 3.1. elPP-g-MA reaches a grafting level of $3.5 \text{ wt}\%$ and its molar mass is clearly reduced in comparison with the starting PP. The degradation of the molar mass is caused by a side reaction, named β -scission, occurring during the functionalization. The crystallinity of elPP-g-MA is strongly reduced with respect to the starting PP, due to the epimerization reaction occurring in the presence of peroxide and NBS. The additive allows the grafting level to be improved while limiting excessive degradation of the molar mass by β -scission [17].

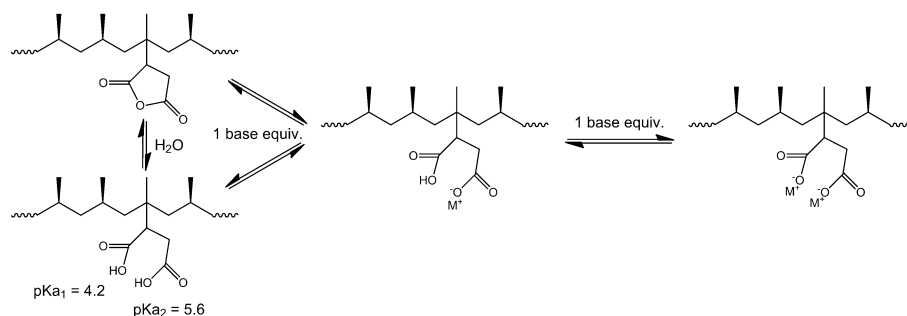


Figure 3.1: PP-g-MA neutralization steps.

3.3.2 Ionomer ND determination

The neutralization reaction can be assessed by FTIR by monitoring the decrease of the carbonyl symmetric stretching vibration of the succinic anhydride band at 1790 cm^{-1} . The asymmetric stretching of the succinic anhydride band is visible at 1864 cm^{-1} but is weaker than the symmetric one. The grafted succinic anhydride moieties can be neutralized twice (Figure 3.1) whereas the first neutralization step is easier because the first acid dissociation constant ($pK_{a1} = 4.2$) is weaker than the second one ($pK_{a2} = 5.6$). After the first neutralization step, the anhydride ring is opened into a carboxylate group and a carboxylic acid. Figure 3.2 shows an enlargement of the carbonyl region of the FTIR spectra of the starting elPP-g-MA and the ionomer neutralized with 0.5 equivalents (equiv.) of 2.5M NaOH solution. The elPP-g-MA spectrum shows only two absorption bands, characteristic for cyclic anhydrides at 1863 cm^{-1} (weak, asymmetrical stretching) and at 1790 cm^{-1} (strong, symmetrical stretching). As shown in Figure 3.2, the intensity of the anhydride bands decreases upon neutralization while two new bands appear at 1715 and 1570 cm^{-1} . These new bands correspond to the carbonyl stretching of carboxylic acid and metal-carboxylate, respectively, [9, 16]. If the ND was calculated on the basis of the decrease of the anhydride band at 1790 cm^{-1} from elPP-g-MA ($A_{anh_{elPP-g-MA}}$) to ionomer ($A_{anh_{ionomer}}$), using Equation 3.1, it would be overestimated

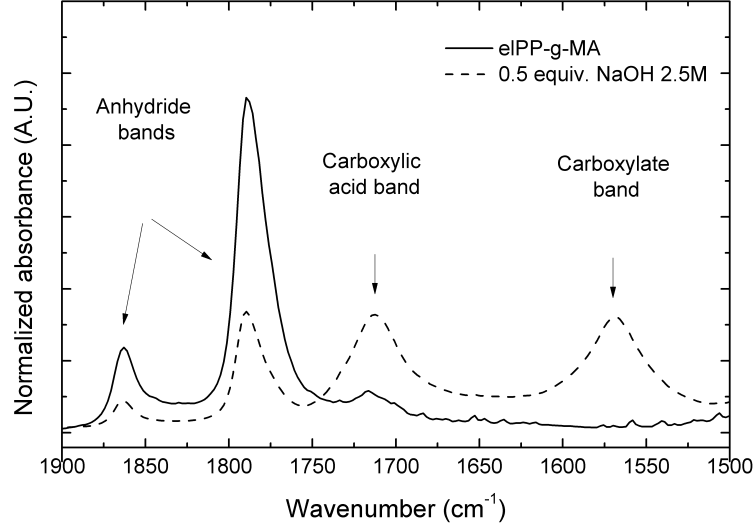


Figure 3.2: Enlargement of the carbonyl region of the FTIR spectra for elPP-g-MA and 0.5 equiv. NaOH 2.5M ionomer.

due to the carboxylic acid functions contribution.

$$ND = \frac{A_{anh_{ionomer}}}{A_{anh_{elPP-g-MA}}} \cdot 100 \quad (3.1)$$

To solve this problem, elPP-g-MA was hydrolyzed in a water atmosphere in order to open properly the anhydride functions into diacids. Figure 3.3 shows an enlargement of the carbonyl region of the FTIR spectra for dry elPP-g-MA (starting material) and wet elPP-g-MA. Wet elPP-g-MA was then melt-pressed into films at 200 °C. By melt-pressing the wet sample during increasing times, the diacid functions progressively closed to form anhydrides (Figure 3.4). The evolution of the acid band area as a function of the anhydride band area for several melt-pressed samples is presented in Figure 3.5. A linear regression, using Equation 3.2, can be used to convert the anhydride band area (A_{anh}) into acid (A_{acid}) in order to calculate a corrected acid band area (A_{acid_corr}). The corrected acid band area is the area of the acid band that would have been measured if all anhydride functions were hydrolyzed into acid

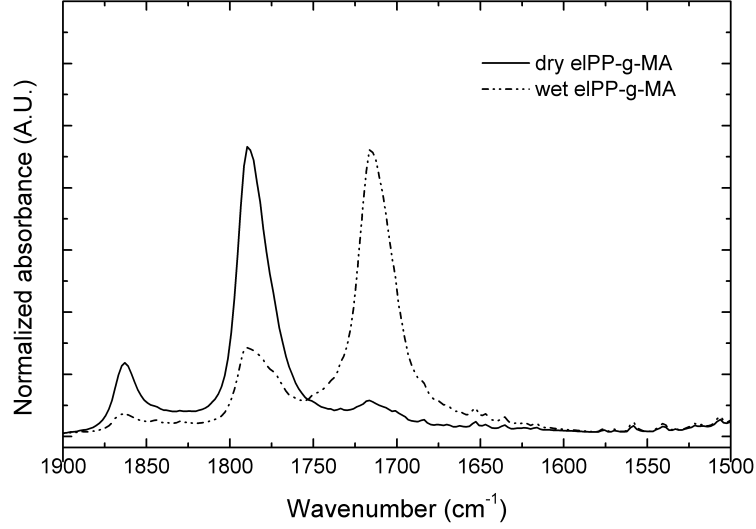


Figure 3.3: Enlargement of the carbonyl region of the FTIR spectra for dry and wet elPP-g-MA.

and this value corresponds to the Y intercept (Y_0) of Equation 3.3. The corrected acid band area can be calculated by measuring the anhydride and acid bands areas of a sample using Equation 3.4. A corrected neutralization degree (cND) based on the decrease of the corrected acid band area from elPP-g-MA ($A_{acid_corr_{elPP-g-MA}}$) to ionomer ($A_{acid_corr_{ionomer}}$) can be calculated using Equation 3.5.

$$A_{acid} = (A_{anh} \cdot S) + Y_0 \quad (3.2)$$

$$A_{acid_corr} = Y_0 \quad (3.3)$$

$$A_{acid_corr} = A_{acid} - (A_{anh} \cdot S) \quad (3.4)$$

$$cND = \frac{A_{acid_corr_{ionomer}}}{A_{acid_corr_{elPP-g-MA}}} \cdot 100 \quad (3.5)$$

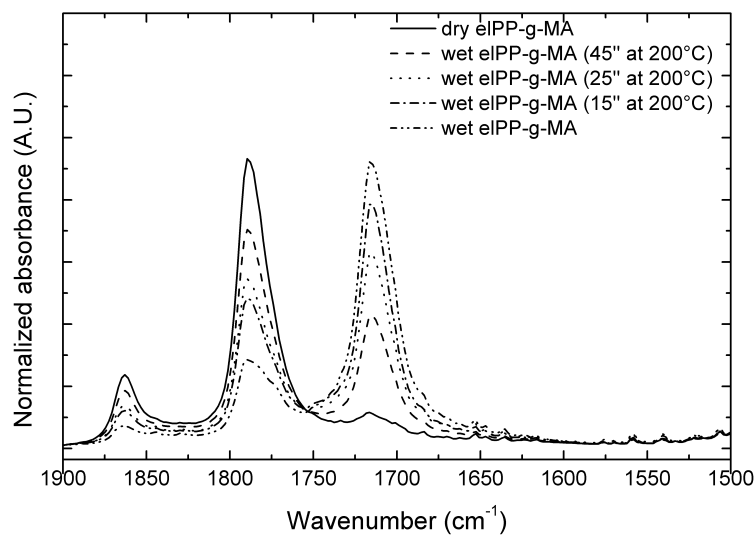


Figure 3.4: Enlargement of the carbonyl region of the FTIR spectra for melt-pressed wet elPP-g-MAs during increasing times.

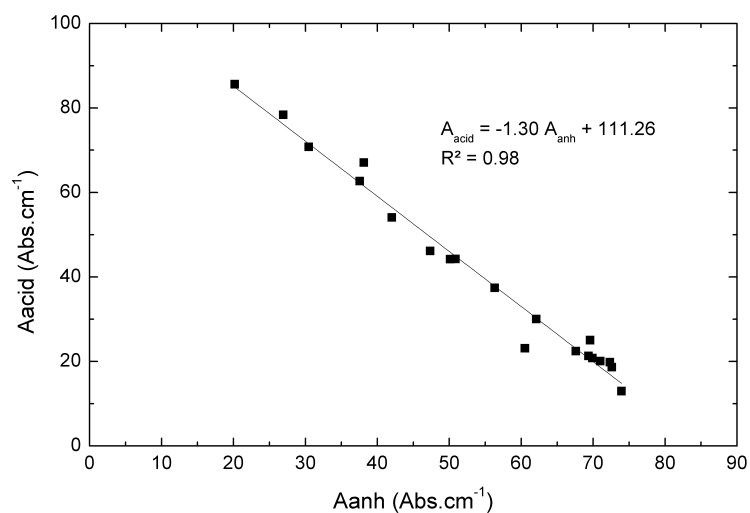


Figure 3.5: Acid band area (A_{acid}) evolution as a function of the anhydride band area (A_{anh}) for the melt-pressed elPP-g-MAs

3.3.3 Influence of the nature of the base on the ND

The influence of the nature of the base on the neutralization degree has been studied. Two different bases were used: sodium hydroxide (NaOH) and sodium acetate (NaAc). These bases were added under various forms to the molten elPP-g-MA. One base equiv. refers to the amount of base required to neutralize all the anhydride functions twice. NaOH was added in 2.5M aqueous solution (NaOH 2.5M) at 0.1, 0.2, 0.3, 0.5 and 0.75 equiv. or as powdered solid (NaOH sol.) at 0.75 equiv. NaAc was added as hydrated solid ($\text{NaAc} \cdot 3\text{H}_2\text{O}$ sol.) and as 2.5 molar aqueous solution (NaAc 2.5M) at 0.1, 0.2, 0.5, 0.75 and 1 equiv. or as anhydrous solid (NaAc anh. sol.) at 1 equiv.

Figure 3.6 shows the evolution of the cND of ionomers, as a function of the added amount of base. Up to 0.2 equiv., the cND is the same for all ionomers, and proportional to the base amount. Differences are observed above 0.2 equiv. The cND of the ionomers synthesized with NaOH 2.5M continues to rise proportionally to the base amount, indicating that the reaction yield is maintained. The cND of the ionomer synthesized with 0.75 equiv. of NaOH sol. is about the half of the one synthesized with 0.75 equiv. of NaOH 2.5M. Over 0.2 equiv., the cND of the ionomers synthesized with $\text{NaAc} \cdot 3\text{H}_2\text{O}$ sol. continues to rise but less importantly than with NaOH 2.5M while the cND of the ionomers synthesized with NaAc 2.5M reaches a plateau. The cND of the ionomer prepared with 1 equiv. of NaAc anh. sol. is 2.7 times lower than the one with 1 equiv. of $\text{NaAc} \cdot 3\text{H}_2\text{O}$ sol. and 1.6 times lower than the one with 1 equiv. of NaAc 2.5M.

The neutralization reaction requires water to ionize the base. Although hygroscopic, NaOH sol. powder contains much less water than NaOH in solution. This explains the observed difference in cND between NaOH 2.5M and NaOH sol. The difference in cND observed between the ionomers neutralized by NaOH and NaAc results from their pKa which are 15.7 for NaOH ($\text{H}_2\text{O}/\text{OH}^-$) and 4.76 for NaAc ($\text{CH}_3\text{CO}_2\text{H}/\text{CH}_3\text{CO}_2^-$). NaOH is a stronger base than NaAc and is

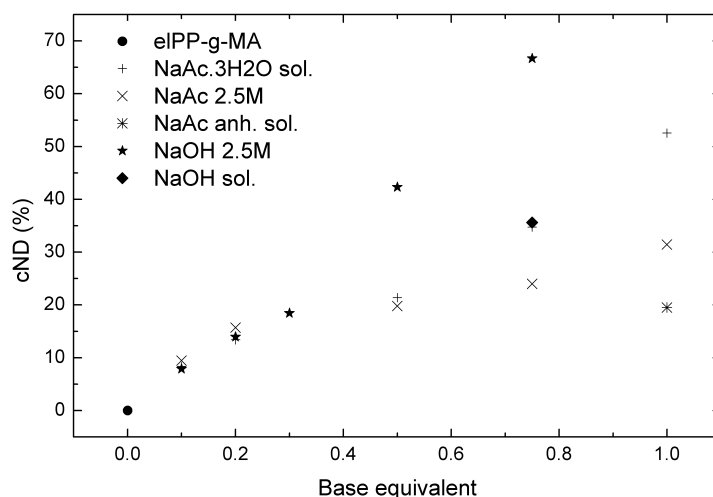


Figure 3.6: Ionomers cND evolution versus base equivalent

therefore more efficient to neutralize elPP-g-MA under the same conditions. Considering the pKa difference between the grafted succinic moieties and the bases, a complete reaction is theoretically expected with NaOH and an equilibrated reaction with NaAc. However, the neutralization reaction is displaced towards the products formation since the reaction residue (H_2O for NaOH, $\text{CH}_3\text{CO}_2\text{H}$ for NaAc) is evaporated during the ionomer synthesis. The difference in cND observed between the ionomers neutralized by $\text{NaAc} \cdot 3\text{H}_2\text{O}$ sol. and NaAc 2.5M cannot be rationalized. As for NaOH, the presence of water, either from salt hydration for $\text{NaAc} \cdot 3\text{H}_2\text{O}$ sol., or from solution for NaAc 2.5M, explains the higher cND obtained when neutralizing elPP-g-MA with a water-containing NaAc salt rather than with NaAc anh. sol. The neutralization efficiency order for all bases is the following: $\text{NaOH 2.5M} > \text{NaOH sol.} \approx \text{NaAc} \cdot 3\text{H}_2\text{O sol.} > \text{NaAc 2.5M} > \text{NaAc anh. sol.}$

The ionomer prepared with 0.75 equiv. of NaOH 2.5M reaches a critical neutralization degree value. When synthesizing this ionomer, the torque increased until the blender-knives broke the ionic network and expeled it. The crosslinking density reaches a plateau and a higher

neutralization degree cannot be obtained. For that reason, the characterization of this sample is omitted.

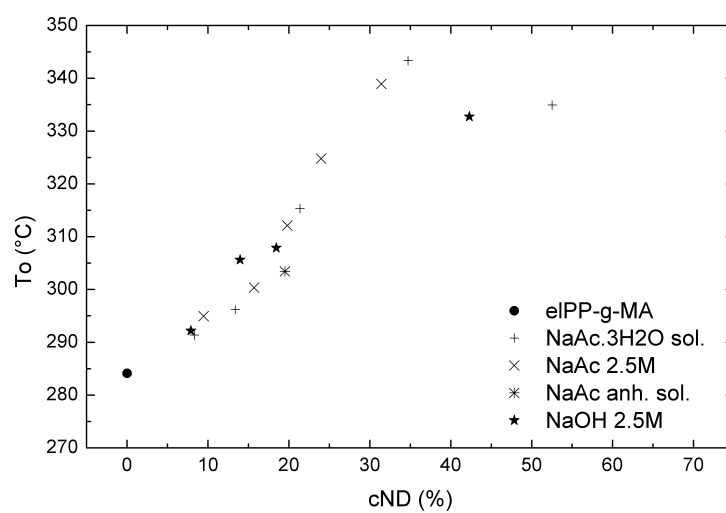
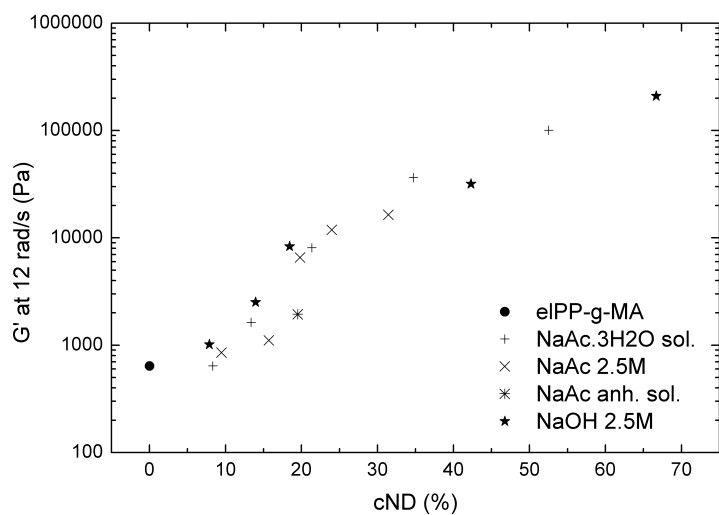
3.3.4 Ionomer characterizations

DSC. While the DSC trace of elPP-g-MA (not shown here, but similar to the one presented by Henry et al. [17]) exhibits a glass-transition around $-4.2\text{ }^{\circ}\text{C}$ and a weak broad melting peak, the DSC traces of the ionomers show only a glass-transition. T_g for all the ionomers are similar to the one of elPP-g-MA.

TGA. Thermogravimetric analysis was performed on the ionomers. In order to compare all the samples, the temperature at 10 % weight loss, which corresponds to the onset of the degradation, is plotted as a function of the cND in Figure 3.7. There is a significant increase in the onset temperature (T_o) with respect to the cND. At high ND, the T_o is measured about $60\text{ }^{\circ}\text{C}$ higher than for elPP-g-MA. This phenomenon can be explained by the ionic crosslinking which holds together the polymer segments resulting from thermal degradation (of the ionomer). As the neutralization degree increases, the crosslinking density increases proportionally. Hence the polymer segments are tied together and the onset temperature is raised.

Rheology. Frequency sweep experiments were performed on all the samples. To facilitate the comparison between the different samples, only the values of shear elastic modulus and complex viscosity, taken at 12 rad/s , are presented³. Figures 3.8 and 3.9 show the evolution of the shear elastic modulus (G') and the complex viscosity (η^*) respectively, as a function of the cND. Both the shear elastic modulus and the complex viscosity increase about 2 decades with the cND. The phenomenon is explained by the matrix reinforcement as a result of the ionic crosslinking. By increasing the neutralization degree, the extent of ionic crosslinking rises and enhances the reinforcement effect.

³Frequency chosen in the terminal region

Figure 3.7: Ionomers onset temperature (T_o) versus cNDFigure 3.8: Ionomers shear elastic modulus (G') at 12 rad/s versus cND

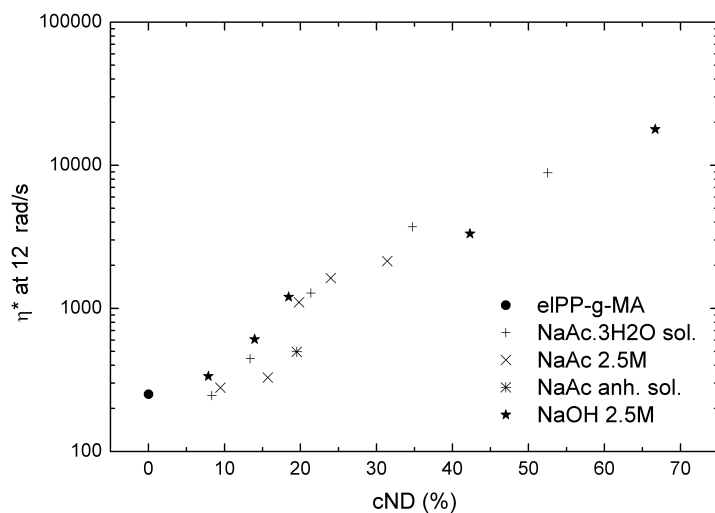


Figure 3.9: Ionomers complex viscosity (η^*) at 12 rad/s versus cND

3.4 Conclusions

Elastomeric highly-functionalized polypropylene-graft-maleic anhydride was produced and characterized. From this material, new carboxylated ionic thermoplastic elastomers of polypropylene were successfully synthesized. Two sodium bases were used under different physical forms to compare their efficiency to neutralize the elastomeric polypropylene-graft-maleic anhydride. It was shown that water, either from salt hydration or from salt aqueous solution, is required to ionize the base in order to allow the acid-base reaction to occur. A method was developed to determine the effective neutralization degree by infrared spectroscopy. The choice of the base has a strong influence on the neutralization degree. Sodium hydroxide allowed the neutralization yield to be kept almost constant even at high neutralization degree. However, as the neutralization yield never reaches 100 %, the excess of the added sodium hydroxide may lead to corrosion. Sodium acetate is a weak base but the neutralization reaction is displaced towards product formation since the reaction residue (acetic acid) is evaporated during the ionomer synthesis.

Furthermore, no corrosion is expected with sodium acetate. For these reasons, sodium acetate is preferred over sodium hydroxide. The ionomer physical properties were improved strongly. The thermal stability in air atmosphere, shear storage modulus and complex viscosity in the flow region were largely increased as a function of the neutralization degree.

Acknowledgments

The authors thank La Région Wallonne and FRIA (Fonds pour la formation à la Recherche dans l'Industrie et dans l'Agriculture) for financial support. J. Marchand-Brynaert is Senior Research Associate of the FRS-FNRS (Fonds National de la Recherche Scientifique, Belgium). Prof. A. Jonas is acknowledged for help and useful discussions about the FTIR fitting routine and Prof. J. Devaux for his kind support.

Appendix to Chapter 3

Assumed mechanism of maleic anhydride grafting onto polypropylene in the presence of N-bromosuccinimide

The assumed mechanism of maleic anhydride grafting onto polypropylene in the presence of N-bromosuccinimide is given in Figure 3.10. The following citation from Henry et al. [17] described this assumed mechanism:

The grafting is expected to be different whether or not NBS is present during the grafting process. In absence of NBS, single or interacting grafts (oligomers or closely grafted anhydride rings) are suspected to be located at or near the chain ends, hence avoiding the PP-g-MA to crosslink upon addition of a diamine. On the other hand, in the presence of NBS, in-chain grafting of single succinic anhydride moieties is suggested. Bromine radicals from NBS decomposition

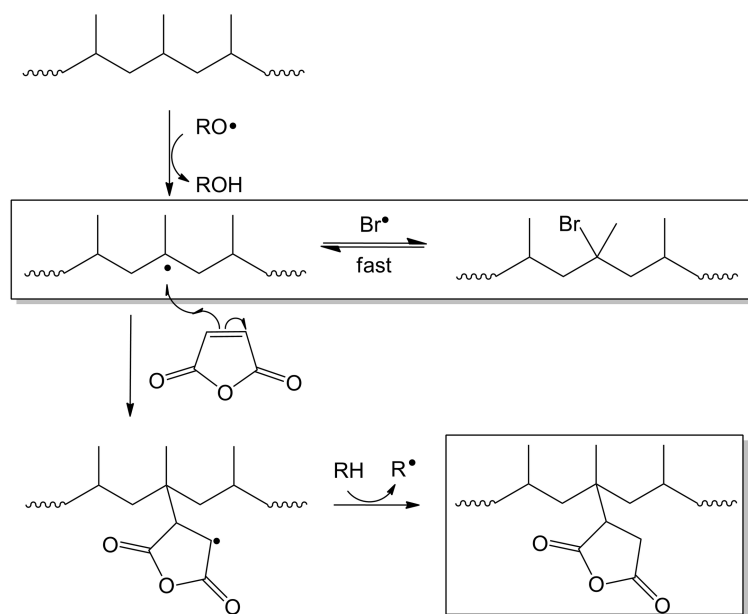


Figure 3.10: Assumed mechanism of maleic anhydride grafting onto polypropylene in the presence of N-bromosuccinimide

are assumed to be responsible for promoting grafting levels, preventing excessive degradation and simultaneously tuning the crystallinity of the PP-g-MA via iPP backbone epimerization.

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Chapter 4

PP-g-MA/Clay Nanocomposites: Optimization of the Compatibilizer

Dans cette partie du travail, nous avons produit des PP-g-MAs aux propriétés contrôlées, c'est-à-dire taux de greffage, masses molaires et cristallinité. Parmi le large éventail des matériaux synthétisés, un PP-g-MA a été sélectionné sur base de sa capacité à disperser l'argile et à conférer au nanocomposite correspondant une meilleure stabilité thermique contre la perte de masse. Ce PP-g-MA appelé "optimisé", sera utilisé dans notre procédé final.

Tuning the functionalization chemistry of Polypropylene for Polypropylene/clay nanocomposites

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To be submitted to Reactive and Functional Polymers.

Work presented at the Ph.D student day Annual Meeting, 2010
(Louvain-la-Neuve, Belgium).

Abstract

New polypropylene(PP)-graft-maleic anhydride (PP-g-MA) samples have been successfully synthesized by adding N-bromosuccinimide (NBS) during the reactive extrusion process. These NBS-mediated PP-g-MAs possess higher graft content than classic PP-g-MAs (i.e. without NBS) while they keep acceptable molar masses. NBS-mediated PP-g-MAs were used as matrices in model PP-g-MA/organoclay nanocomposites and compared with commercial and home-made classic PP-g-MAs in order to evaluate their ability to disperse the clay. Significant better degrees of clay delamination and dispersion were reached using NBS-mediated PP-g-MAs than with classic PP-g-MAs. As expected, PP-g-MAs having high graft content showed the best clay dispersion. Within the examined range of molar masses, the PP-g-MA molar mass had no influence on the clay dispersion. However, PP-g-MAs presenting important reduction of crystallinity displayed poor clay dispersion even if they have high graft content. The PP-g-MA/organoclay nanocomposite prepared using the selected “optimized” NBS-mediated PP-g-MA exhibited the best improvement of thermal properties and one of the best clay dispersions. PP/PP-g-MA blends were prepared to evaluate the miscibility between PP and selected PP-g-MAs. No problem of miscibility between the selected NBS-mediated PP-g-MA and PP was noticed. Finally the

PP/organoclay prepared using the selected NBS-mediated PP-g-MA as compatibilizer showed much better clay dispersion and thermal stability than the one prepared with the corresponding classic PP-g-MA, thus establishing the interest to use such new NBS-mediated PP-g-MAs as compatibilizers.

4.1 Introduction

Polymer/clay nanocomposites have become fashionable during the last decades due to properties enhancement obtained with the addition of just a few percents of filler. In such materials, one can expect higher mechanical and barrier properties, flame retardant behavior while the material transparency is preserved [1–4]. For obtaining polymer/clay nanocomposites, clay layers which are naturally stacked into aggregates of several microns, need to be separated and dispersed into the polymer matrix. The more separated and dispersed the clay layers are, the higher the surface area for polymer/filler interactions and the better the overall properties enhancements are. Several ways exist to synthesize polymer/clay nanocomposites but the most usual is by melt-blending since this method is inexpensive, environment-friendly and straightforward [4–6]. Due to the lack of compatibility between most polymers and clays, nanocomposites made by melt-blending are synthesized almost exclusively from organoclays [1, 2, 5, 7]. In organoclays, organic cationic surfactants, generally alkylammoniums, replace the sodium interlayer cations of the native clay [7]. The introduction of surfactants increases the interlayer spacing and lowers the clay surface energy which facilitates separation and dispersion of the clay layers into the polymer matrix.

Polypropylene (PP) is one of the most successful thermoplastic polymers due to its attractive combination of properties such low density, high thermal stability, resistance to corrosion and low cost. PP is consequently of a very large commercial importance and dominates a lot

of industrial applications. It is then not surprising that PP is one of the most used matrices in polymer/clay nanocomposites. PP/clay nanocomposites are usually prepared by melt-blending, with organoclays and compatibilizers such as PP-graft-maleic anhydride (PP-g-MA) [8–10]. Compatibilizers are indeed required due to the huge polarity difference between the polyolefin matrix and the clay. PP-g-MA allows wetting of the clay surface by hydrogen-bond interactions between the anhydride functions (in fact, carboxylic acids after hydrolysis) and the oxygen atoms at the surface of the silicate layers [11, 12].

Even when using organoclay and compatibilizers, PP/clay nanocomposites usually exhibit modest clay dispersion and consequently limited properties improvements are obtained. The main reason is the poor thermal stability of the alkylammonium-surfactants which decompose at extrusion temperatures leading to a collapse of the silicate layers [13–15]. Another important reason is that the commercial PP-g-MAs have a low MA content which limits consequently the interactions between the clay and the compatibilizers. Indeed, PP-g-MAs are commonly synthesized through reactive extrusion using peroxide and MA, and the unavoidable β -scission reactions of the PP chains impose to limit the grafting to quite low contents in order to maintain PP molar masses compatible with acceptable mechanical properties. As a result, two categories of commercial PP-g-MAs exist. Table 4.1 shows the properties of some commercial PP-g-MAs that were studied and compared in the literature, as matrices or compatibilizers for the elaboration of PP/clay nanocomposites. A detailed description of these results is available in supporting information. In the first category are the usual so-called “classic” PP-g-MAs with low MA content and still a high molar mass (typically MA content [MA] < 1 wt%, number average molar mass (M_n) > 10 kg/mol and weight average molar mass (M_w) > 40 kg/mol). In the second category are PP-g-MAs oligomers or PP-g-MA waxes with high MA content and a very low molar mass (typically [MA] > 1 wt%, M_n < 10 kg/mol and M_w < 40 kg/mol). Low-MA PP-g-MAs offer few

interactions with clay but good miscibility with PP and good mechanical properties of the composite are thus expected. High-MA PP-g-MAs offer more interactions with clay but present immiscibility drawbacks with PP [8, 9, 16, 17]. Moreover the resulting composites exhibit poor mechanical properties since they are brittle. The mechanical properties and the miscibility of PP/PP-g-MA blends explain that low-MA PP-g-MAs are mainly used as compatibilizers in PP/clay nanocomposites instead of high-MA PP-g-MAs.

These studies (see Table 4.1) clearly pointed out the need to use a PP-g-MA compatibilizer featuring the optimal functionalization of the PP chains to facilitate the intercalation, but not exceeding a certain level of MA content to avoid PP/PP-g-MA immiscibility. Recently, a new method to synthesize highly functionalized polyolefins, using a bromine compound (mainly N-bromosuccinimide; NBS) during the reactive extrusion process has been developed [29, 30]. High levels of grafted maleic anhydride can be reached (up to 2.5 – 3 wt.%) without forming grafted PP waxes.

The present paper discusses the fine tuning of PP-g-MA synthesis for the preparation of model PP-g-MA/clay nanocomposites and PP/clay nanocomposites. The required PP-g-MAs have the following specifications: (1) higher MA content than usual low-MA PP-g-MAs for better interactions with clay, without reaching the miscibility limit with PP; (2) acceptable molar mass to keep good mechanical properties. Accordingly, a series of NBS-mediated PP-g-MAs was prepared by reactive extrusion, characterized and compared with classic PP-g-MAs (i.e. without NBS). Classic and NBS-mediated PP-g-MAs were then used as matrices to elaborate model PP-g-MA/organoclay nanocomposites in order to evaluate their capacity of clay dispersion. An organoclay, modified by bis(2-bis hydroxyethyl) methyl tallow ammonium (Cloisite 30B) and recommended for polar matrices such as polyamides, was used instead of organoclay modified by dimethyl-ditallow ammonium especially designed for polyolefin matrices, in view to investigate more accurately the

Table 4.1: Properties of commercial PP-g-MAs studied from literature. Legend: [acid] is the acid value, [MA] is the maleic anhydride content, Mn and Mw are the number and weight average molar masses and MFI is the melt flow index.

PP-g-MA	[acid] (mgKOH/g)	[MA] (wt.%)	Mn (kg/mol)	Mw (kg/mol)	MFI (g/10 min)	Supplier	References
Epolene E43	47	3.8-4	3.9	9.1	1654 (180 °C)	Eastman	[18-22]
Epolene E43		2.9 ^a	8.8 ^a			Eastman	[23]
Exxcelor PO2011		0.3			162 (230 °C)	Exxon	[24]
HMPP		1.9		185			[25]
Hostaprime HC5		4.2	4			Hoechst	[23]
LMPP		1.8		59			[25]
Licomont AR504		3.5-4	1.5-2.9		wax	Clariant	[24, 26]
Polybond PB3000		1.2			425 (190 °C)	Crompton	[18, 22]
Polybond PB3001		0.1		270	5.1 (190 °C)	Crompton	[27]
Polybond PB3002		0.6 ^a			12 (230 °C)	Crompton	[24]
Polybond PB3150		0.5		330	20 (190 °C)	Crompton	[18-22]
Polybond PB3150		1.3 ^a			43 (230 °C)	Crompton	[24]
Polybond PB3200		1		120	115 (190 °C)	Crompton	[18, 22, 27]
PPMA-110TS	7	0.6 ^b		12		Sanyo	[28]
PPMA-1010	52	4.6 ^b		30		Sanyo	[8, 9, 28]
PPMA-1001	26	2.3 ^b		40		Sanyo	[8]
Scona TPPP 2112 FA		1	200-300			Krometra	[26]

^a the origin of these data is not described; however manufacturer's data are the following: E43 [MA] = 3.8 wt. % and Mw = 9.1 kg/mol; PB3002 [MA] = 0.2 wt.%; PB3150 [MA] = 0.5 wt. %

^b value calculated from [acid].

tuning of the PP-g-MA on clay dispersion. Indeed, since Cloisite 30B is much more difficult to disperse into polyolefins, more important differences of clay dispersion and properties are expected when tuning the PP-g-MA than with organoclay designed for polyolefins. The influence of the PP-g-MA characteristics on organoclay dispersion have been fully discussed. Finally, PP/organoclay nanocomposites have been prepared and characterized using selected optimized PP-g-MAs.

4.2 Experimental

4.2.1 Materials

PP Moplen HF500N (MFI = 12 g/10 min) was purchased from Basell. The free radical initiator was Luperox 101 XLS 50 from Arkema (2,5-bis(tert-butyl-peroxy)-2,5-dimethylhexane, labeled DHBP, 50 wt.% blend with silica). Maleic anhydride (MA, Acros, 99 % purity), *N*-bromosuccinimide (NBS, Acros, 99 % purity) and toluene (Fisher, analytical grade) were used as received. Tetrabutylammonium hydroxide (TBAOH) 0.1 N in toluene-methanol was purchased from Merck and bromothymol blue came from Sigma. Sodium-Montmorillonite modified with bis(2-bis hydroxyethyl) methyl tallow ammonium chloride (Cloisite 30B, labeled C30B) was purchased from Southern Clay Product. Two commercial PP-g-MAs were used for comparison: Polybond 3200 (1 wt.% of MA [manufacturer's data], labeled Plb) purchased from Chemtura and Licocene 7452 (3.6 wt.% of MA [value calculated from [acid] = 41 mg_{KOH}/g, manufacturer's data], labeled Lico) supplied by Clariant. All reagents were used without further purification.

4.2.2 Sample preparation

Synthesis of PP-g-MAs

PP-g-MAs were synthesized by reactive extrusion in a Brabender single screw extruder equipped with a feeding screw of $L/D = 20$. The bar-

rel temperature is fixed at 200 °C and the screw speed is set to 30 RPM, which allowed a residence time of about 1 minute. PP-g-MAs' compositions are presented in Table 4.2. PP, MA, DHBP and NBS were dry-mixed and then poured into the hopper of the extruder and resulting PP-g-MAs' yarns were poured into cold water and cryo-ground with a pulverisette 14 mill from Fritsch. The decomposition half-time of DHBP at 200 °C is 6 s. The highly functionalized elastomeric PP-g-MA eIP (Table 4.2) has been synthesized by following the procedure described by Henry et al. in order to maximize the grafting level [29–31]. PP-g-MAs 1 to 5 are called “classic” PP-g-MAs and are synthesized using PP, AM and DHBP. PP-g-MAs 1 to 3 differ by the amount of peroxide (DHBP), PP-g-MAs 2, 4 and 5 differ by the amount of introduced MA. PP-g-MAs 6 to 10 are called “NBS-mediated PP-g-MAs” and are synthesized from PP, AM, peroxide and NBS. PP-g-MAs 6 to 8 differ by the amount of NBS and PP-g-MAs 7, 9 and 10 differ by the amount of MA. DHBP and NBS amounts are calculated via the active bromine to active oxygen ratio ($Br\bullet/O\bullet$) which is defined as the maximum concentration of bromine free radicals ($Br\bullet$) that could be produced over the maximum concentration of active oxygen-based free radicals ($O\bullet$) produced by the organic peroxide [29] (see Equations 4.1, 4.2, 4.3 and 4.4 in supporting information). The use of $O\bullet$ and $Br\bullet$ to calculate the amount of peroxide and bromine compound is more universal since it is independent of the peroxide or bromine compound used. The choice of $O\bullet$ and $Br\bullet$ values for the synthesis of these PP-g-MAs is based on the in-house expertise on the NBS-mediated synthesis of PP-g-MA.

Synthesis of PP-g-MA references and nanocomposites

PP-g-MA references (PP-g-MAs re-extruded without clay) and PP-g-MA/clay nanocomposites (PP-g-MAs blended with about 5 wt.% of C30B in inorganic content) samples were prepared in a DSM Xplore 15 ml microcompounder. The samples were extruded at a screw speed of 200 RPM at 200 °C during 2 minutes. References are labeled R1 to

Table 4.2: Composition of the reactive media for PP-g-MA synthesis.

PP-g-MAs	MA (wt.%)	DHBP (wt.%)	NBS (wt.%)	$O\bullet$ (%)	$Br\bullet$ (%)	$Br\bullet/O\bullet$
elP	5	1.63	0.8	0.36	0.36	1
1	5	0.23	0	0.05	0	/
2	5	0.45	0	0.1	0	/
3	5	0.91	0	0.2	0	/
4	1	0.45	0	0.1	0	/
5	3	0.45	0	0.1	0	/
6	5	0.45	0.07	0.1	0.03	0.3
7	5	0.45	0.09	0.1	0.04	0.4
8	5	0.45	0.11	0.1	0.05	0.5
9	1	0.45	0.09	0.1	0.04	0.4
10	3	0.45	0.09	0.1	0.04	0.4
2*	5	0.45	0	0.1	0	/
7*	5	0.45	0.09	0.1	0.04	0.4

R10 and nanocomposites NC1 to NC10 (Table 4.3), with the number corresponding to the synthesized PP-g-MA in Table 4.2. For comparison, Plb and Lico were also extruded with and without C30B (labeled RPlb, RLico, NCPlb and NCLico).

Preparation of PP/PP-g-MA blends

PP/20 wt.% elP blend (BeP-20) was prepared in a Brabender Plasticorder equipped with an electrically heated W50EH mixing device of 50 cm³ capacity, during 5 minutes. The mixing speed was set to 100 RPM and the temperature at 220 °C. Samples are then quenched at ambient temperature. Other PP/PP-g-MA were prepared in a DSM Xplore 15 ml microcompounder. The samples were extruded at a screw speed of 200 RPM at 200 °C during 2 minutes. Blends are labeled by adding the letter “B” before the PP-g-MA code, following by the weight fraction of PP-g-MA into PP (Table 4.3).

Table 4.3: Composition of PP-g-MA references (R), PP/PP-g-MA blends (B), PP-g-MA/C30B and PP/C30B nanocomposites (NC).

Samples	PP-g-MA	PP (wt.%)	PP-g-MA (wt.%)	C30B (wt.%)
RPlb	Plb	0	100	0
RLico	Lico	0	100	0
R1	1	0	100	0
R2	2	0	100	0
R3	3	0	100	0
R4	4	0	100	0
R5	5	0	100	0
R6	6	0	100	0
R7	7	0	100	0
R8	8	0	100	0
R9	9	0	100	0
R10	10	0	100	0
NCPlb	Plb	0	93.4	6.6
NCLico	Lico	0	93.4	6.6
NC1	1	0	93.4	6.6
NC2	2	0	93.4	6.6
NC3	3	0	93.4	6.6
NC4	4	0	93.4	6.6
NC5	5	0	93.4	6.6
NC6	6	0	93.4	6.6
NC7	7	0	93.4	6.6
NC8	8	0	93.4	6.6
NC9	9	0	93.4	6.6
NC10	10	0	93.4	6.6
BelP-20	eIP	80	20	0
BPlb-10	Plb	90	10	0
BLico-10	Lico	90	10	0
B2-10	2	90	10	0
B2-20	2	80	20	0
B7-10	7	90	10	0
B7-20	7	80	20	0
RPP2*	2*	90	10	0
RPP7*	7*	90	10	0
NCP2*	2*	83.7	9.3	7
NCP7*	7*	83.7	9.3	7
NCPPlb	Plb	79	15	6

Synthesis of selected PP-g-MA and of PP-based references and nanocomposites

In order to synthesize PP/PP-g-MA/clay nanocomposites, selected PP-g-MAs were prepared at a large scale on a co-rotating twin-screw extruder Brabender Clam Shell TSE 20/40. The extruder screw length is 800 mm with a L/D ratio of 40. The barrel temperature is fixed at 200 °C, the screw speed is set to 40 RPM and the throughput is around 2 kg/h. These conditions were determined to reach approximatively the same residence time than on the Brabender single screw extruder. The extruded samples were immediately quenched into cold water and cryo-ground. Scale-up synthesized PP-g-MA are labeled using the same number but with additional “*” (i.e. 2*, Table 4.2).

PP/clay nanocomposites were prepared by direct melt blending of PP, 10 wt.% of PP-g-MA and 5 wt.% of C30B in inorganic content, in a co-rotating twin-screw extruder Krupp WP ZSK25. The extruder screw length is 1000 mm with a L/D ratio of 40. The barrel temperature is fixed at 200 °C. The throughput is fixed at 7 kg/h and the screw speed at 200 RPM. The extruded samples were immediately quenched into cold water and pelletized. References are labeled RPP2* and RPP7* and nanocomposites NCPP2* and NCPP7* (Table 4.3). Sample NCPP1b was introduced for comparison.

4.2.3 Characterizations

Quantification of the grafted species. Prior to analysis, PP-g-MA sample is dissolved into refluxing toluene (about 5 g of PP-g-MA into 300 ml of toluene) and precipitated into a large excess of cold acetone, filtered and dried under vacuum at 90 °C overnight. Anhydride contents were determined according to a titration procedure [32]. Washed PP-g-MA sample is dissolved into 150 ml of refluxing toluene and five drops of 1% (w/v) bromothymol blue in methanol were added. PP-g-MA solution is then titrated by adding tetrabutylammonium hydroxide (TBAOH) solution and the titration is stopped at the visual

endpoint when the colour change was stable.

Differential scanning calorimetry (DSC). The analyses were performed on a Mettler Toledo DSC 821e using a first heating ramp from 20 to 220 °C followed by a cooling ramp from 220 to 20 °C. The heating/cooling rate of each segment was 10 °C/min. The role of the first heating run is to erase the thermal history of the sample. The crystallization temperature (T_c) and the enthalpy of crystallization (ΔH_c) were measured on the cooling ramp. ΔH_c is calculated per gram of polymer and the crystallinity percentage (X_c) by dividing the sample enthalpy of crystallization by theoretical fusion enthalpy of 100 % crystalline isotactic PP = 207 J/g [33]. DSC was calibrated with indium and zinc before use.

Size exclusion chromatography (SEC). Molar masses were determined on a Waters Alliance GPCV 2000 equipped with two Styragel HT 6E and one Styragel HT 2 columns along with a differential refractometer. The mobile phase was 1,2,4-trichlorobenzene (TCB) stabilized with 2 % of Irganox 1010. The concentration of the sample was 2 mg/mL in TCB and dissolution was achieved at 145 °C. The injection volume was 215 μ L. Temperature was held constant at 145 °C throughout the analysis. The system was calibrated prior to the analysis with polystyrene (PS) standards.

Transmission electron microscopy (TEM). Samples were ultra-microtomed at ambient temperature with a Reichert Microtome and collected on a 300 mesh copper grid. TEM pictures were recorded with a LEO 922 microscope operating at 200 kV. Clay dispersion of nanocomposites was evaluated on ultra-microtomed samples without staining while PP/PP-g-MA blends were stained on copper grid with RuO_4 vapor during 15 minutes.

Atomic force microscopy (AFM). Measurements on PP/PP-g-MA blends were performed with a Nanoscope IV. All scans were performed in air with commercial Si Nanoprobes SPM tips for tapping mode. Phase imaging was performed in tapping mode at the fundamen-

tal resonance frequency of the -Si cantilever with typical scan rates of 16.1 $\mu\text{m/s}$ using j-type scan head. The free oscillating amplitude was 2.0 V.

X-ray diffraction (XRD). The clay interlayer spacing of the nanocomposites was measured by XRD on a Bruker D8 Advance diffractometer using $\text{CuK}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) at 40 kV and 30 mA. XRD patterns of commercial PP-g-MA/clay nanocomposites (NCPlb and NCLico) were recorded with a θ - 2θ goniometer (D5000 from Siemens; radius of the goniometer = 30 cm) using $\text{CuK}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$), a graphite secondary monochromator and a scintillation counter.

Thermogravimetric analysis (TGA). The thermal stability of the references and composites was studied by TGA. The analyses were performed on a Mettler Toledo TGA/SDTA 851e using a heating rate of 20 $^{\circ}\text{C/min}$ under air or nitrogen atmosphere (100 ml/min) from 25 to 1000 $^{\circ}\text{C}$. TGA results are presented as temperatures at 5% (T-5) weight loss under air atmosphere and each value is the average of minimum 3 experiments. T-5 is usually considered as the initial decomposition temperature.

4.3 Results and discussion

4.3.1 Preliminary results on NBS-mediated PP-g-MAs

Highly functionalized elastomeric PP-g-MA (elP) has been synthesized following the procedure described by Henry et al. [29–31] in order to maximize the grafting level. The [MA] of elP reaches 3.5 wt% and its M_n and M_w are significantly reduced in comparison with the native PP (Table 4.4). The drop of molar mass is caused by β -scission reactions occurring during the functionalization. Simultaneously to MA grafting, the use of a bromine compound such as NBS modifies the PP crystallinity via an epimerization reaction of the PP backbone. As a result, the crystallinity of elP is strongly affected (Table 4.4). Nevertheless, the NBS-process allows the grafting level to be improved while

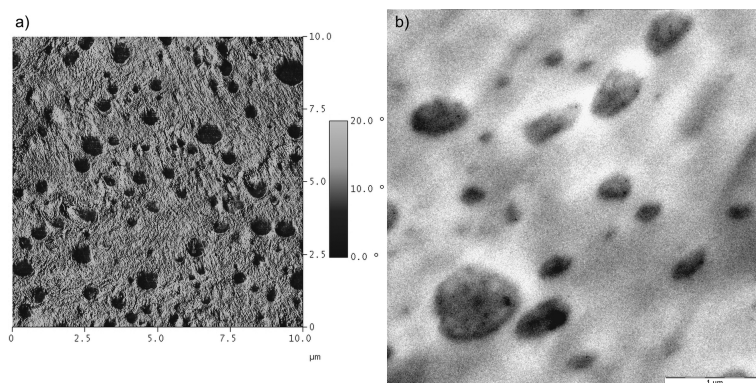


Figure 4.1: AFM (a) and TEM (b) pictures of BelP-20 sample (PP/elP blend containing 20 wt.% of PP-g-MA elP).

limiting excessive diminution of the molar mass [29].

As elP was highly functionalized and had elastomeric behavior, its miscibility into PP was investigated. Figure 4.1 shows AFM and TEM pictures of PP/elP blend (BelP-20) containing 20 wt.% of elP. elP particles sizing between 0.1 and 1 μm are dispersed in the PP matrix, thus clearly indicating that elP is not miscible with PP. Similar structures were observed by Lee et al. for PP toughened with an ethylene-octene elastomer [34]. Although such PP/elP blends could be interesting for applications where toughness is desired, elP immiscibility with PP makes elP a bad candidate to be used as compatibilizer for PP/clay nanocomposites.

4.3.2 Classic and NBS-mediated PP-g-MAs

elP was synthesized using high concentration of peroxide and NBS (1.63 wt.% of peroxide, $O\bullet = 0.36\%$ and 0.8 wt.% of NBS, $Br\bullet = 0.36\%$). By adapting the amounts of peroxide and NBS, it should be possible to avoid too high MA grafting and elastomeric behavior, and to keep acceptable molar masses. The characteristics of PP-g-MAs synthesized using low NBS amounts (“NBS-mediated PP-g-MAs”) will be compared to classic PP-g-MAs synthesized without NBS. Amounts

Table 4.4: Characterization of PP-g-MAs: [MA] is the concentration of grafted maleic anhydride; T_c , ΔH_c and X_c are the temperature and the enthalpy of crystallization and the crystallinity degree, respectively; M_n and M_w are the number and weight average molar masses.

PP-g-MA samples	[MA] (wt%)	T_c (°C)	ΔH_c (J/g)	X_c (%)	M_n (kg/mol)	M_w (kg/mol)
PP	/	124	99	48	46	220
Plb	0.4	113	96	47	25	72
Lico	2.2	109	93	45	7	16
eIP	3.5	83 ^a	3 ^a	2	18	63
1	0.5	113	97	47	21	76
2	0.8	114	94	45	18	53
3	1.2	114	93	45	16	41
4	0.6	113	100	48	21	60
5	0.8	113	97	47	18	48
6	1.0	114	91	44	16	46
7	1.7	114	88	43	15	42
8	2.2	109	82	39	17	52
9	0.7	78	45	22	23	67
10	2.1	100	69	33	15	41
2*	0.5 ^b	119	97	47	24	90
7*	1.2 ^b	115	83	40	12	33

^a data measured from the second heating ramp (no crystallization on the cooling ramp).

^b estimation using FTIR-Titration calibration (see supporting information).

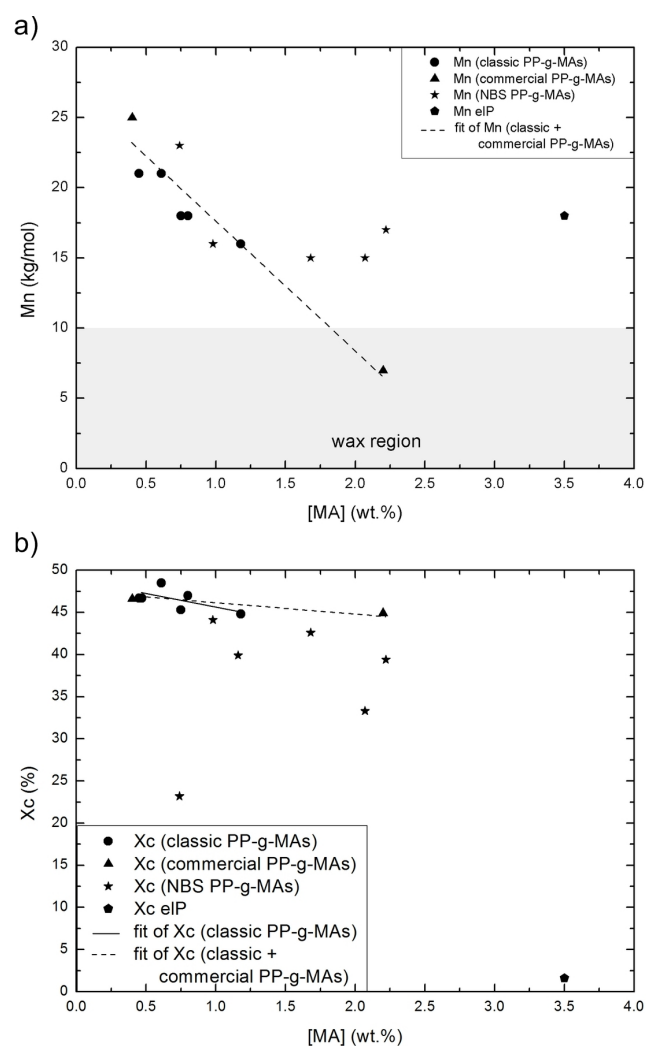


Figure 4.2: Evolution of (a) the number average molar mass (M_n) and of (b) the crystallization degree (X_c) of the PP-g-MAs with the grafting level ($[MA]$). Classic PP-g-MAs are PP-g-MAs 1 to 5, commercial PP-g-MAs are Plb and Lico, and NBS-mediated PP-g-MAs are PP-g-MAs 6 to 10.

of 5 wt.% MA and between 0.1 to 1 wt.% DHBP are frequently used when synthesizing classic PP-g-MA through reactive extrusion [35–44]. Table 4.4 shows the characteristics of classic PP-g-MAs (1 to 5) and of NBS-mediated PP-g-MAs (6 to 10) in comparison with native PP, and two commercial PP-g-MAs (Plb and Lico). Figure 4.2 summarizes the previous results by showing the evolutions of the number average molar mass (M_n) and crystallization degree (X_c) of the PP-g-MAs with their grafting level ($[MA]$).

Regarding the fit of M_n (dotted line) for classic and commercial PP-g-MAs in Figure 4.2a, it is clear that high $[MA]$ cannot be reached without recovering waxes. The amount of peroxide is the limiting factor when synthesizing classic PP-g-MAs. Characteristics (Table 4.4) of classic PP-g-MAs 1 to 5 are quite similar to those of Plb commercial PP-g-MA while the characteristics of Lico commercial PP-g-MA wax would correspond to classic PP-g-MA synthesized using higher peroxide content than in the present study. Our results agree with the observations previously reported in literature [36, 37, 42].

The use of small amounts of NBS allows to obtain high $[MA]$ (up to 2–3 times higher than classic PP-g-MAs) while avoiding PP-g-MA M_n to fall in the wax region ($M_n < 10$ kg/mol). However, the amount of NBS must be carefully adapted to the amounts of MA and peroxide reagents in order to avoid an important drop of PP-g-MA crystallinity (Table 4.4). Indeed, only “optimum” amounts of NBS (see Table 4.2) allow to keep the crystallinity of NBS-mediated PP-g-MAs comparable to the classic and commercial PP-g-MAs, regarding the fit of X_c (dotted line in Figure 4.2b). In comparison, Henry et al. [29, 30] employed about 10 to 20 times more NBS amounts, thus explaining the strong reduction of crystallinity obtained for eIP.

4.3.3 PP-g-MA-/Clay nanocomposites

Structural characterization

The home-made PP-g-MAs 1 to 10 were used as matrices for preparing model PP-g-MA/clay nanocomposites. The nanocomposites were characterized by XRD and TEM to examine the clay basal spacing and the clay dispersion into the polymer, respectively. Model PP-g-MA/clay nanocomposites were also prepared using Plb and Lico commercial PP-g-MAs as matrices (NCPlb and NCLico) for comparisons.

Figure 4.3 shows the X-ray diffraction patterns of the native clay (C30B) and of nanocomposites from commercial, classic and NBS-mediated PP-g-MAs. C30B exhibits only a (001) basal spacing centered at 1.9 nm ($4.7^\circ 2\theta$). All PP/C30B nanocomposites show their main basal spacing shifted from 1.9 to 1.5 nm (4.7 to $6.0^\circ 2\theta$) and an increase of their diffraction intensity in the region of low angles. The basal spacing shift indicates that part of the C30B silicate layers is collapsed due to the surfactant degradation, [19, 45] while the increase of intensity toward low angles is commonly attributed to completely dispersed clay layers [8, 18].

Figure 4.3a suggests that NCPlb possesses a mixed distribution of well dispersed clay layers and collapsed clay stacks while NCLico presents only well distributed clay platelets.

XRD patterns of NC1, NC2 and NC3 (Figure 4.3b) exhibit additional shouldering around 3.2 nm ($2.5 - 3^\circ 2\theta$) indicating that part of the C30B layers have been intercalated. Increasing clay dispersion is expected in the way $NC1 \approx NC4 < NC2 < NC5 \approx NC3$, as deduced from the diffraction intensities toward low angles.

Except for NC9, the peak at 1.5 nm is less intense for nanocomposites obtained from NBS-mediated PP-g-MAs (Figure 4.3c), meaning that less C30B layers have collapsed. NC7 and NC8 show higher increase of their diffraction intensity toward low angles than NC6, NC9 and NC10, while NC9 exhibit a broad and intense peak around $5.5 - 6^\circ 2\theta$. The best clay dispersion among NBS-mediated PP-g-MAs is expected for NC7

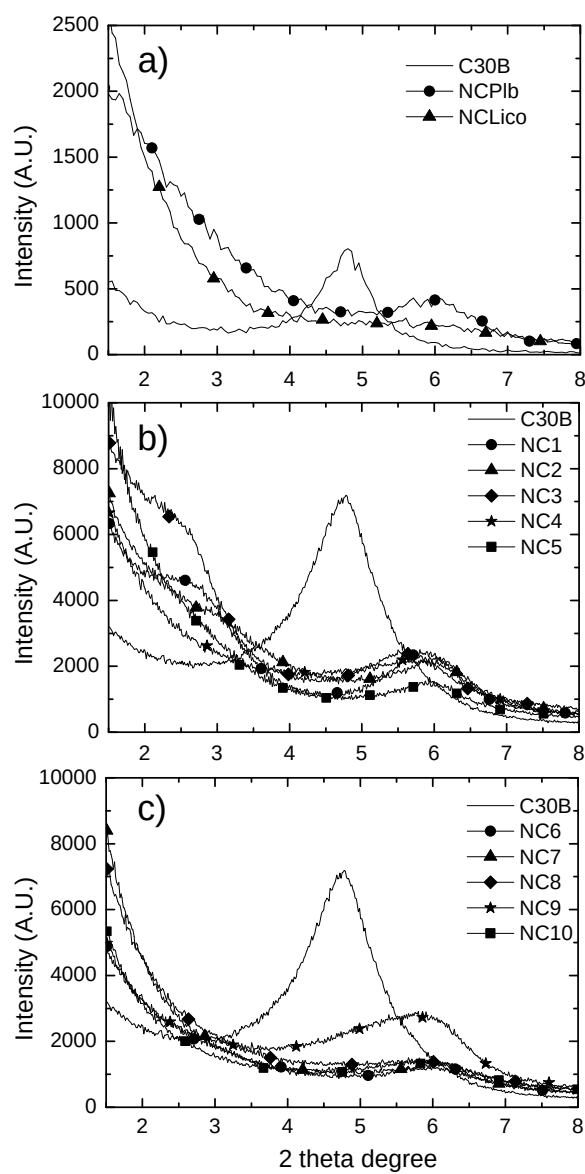


Figure 4.3: XRD patterns of C30B and of PP-g-MA/clay nanocomposites from a) commercial, b) classic and c) NBS-mediated PP-g-MAs.

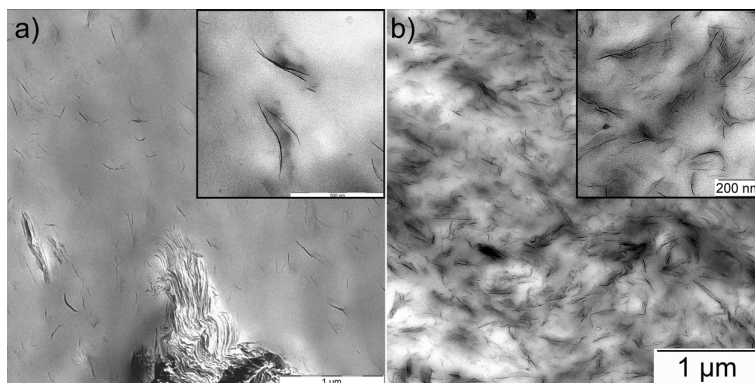


Figure 4.4: TEM pictures of PP-g-MA/C30B nanocomposites from commercial PP-g-MA: NCPIb (a) and NCLico (b).

and NC8.

TEM pictures of nanocomposites from commercial PP-g-MA (Figure 4.4) show a highly heterogeneous morphology for NCPIb, composed of huge clay aggregates and few individual clay platelets while the clay platelets are almost all individualized for NCLico.

In home-made (classic and NBS-mediated) PP-g-MAs nanocomposites (Figures 4.5 and 4.6), black cluster structures can be observed (see for example in the bottom left corner of NC1 TEM picture, Figure 4.5a) due to residual silica supporting the peroxide (DHBP is 50 wt.% supported on silica). Increasing clay dispersion is visible in the way $NC1 < NC4 < NC2 < NC5 \approx NC3$, thus confirming the XRD analyses. NC1 exhibits a similar clay dispersion than NCPIb, while NC3 shows the best clay dispersion among nanocomposites from classic PP-g-MAs with almost all clay layers homogeneously individualized. The clay dispersion of NCLico remains however better than the one of NC3.

NC6, NC7 and NC8 (Figures 4.6a, b and c) show mainly individual clay platelets well distributed with very few clay stacks and the density of individualized clay layers increases in the way $NC6 < NC7 < NC8$. The clay dispersions of NC7 and NC8 are comparable to NC3 and NCLico, respectively. NC9 and NC10 (Figures 4.6d and e) exhibit

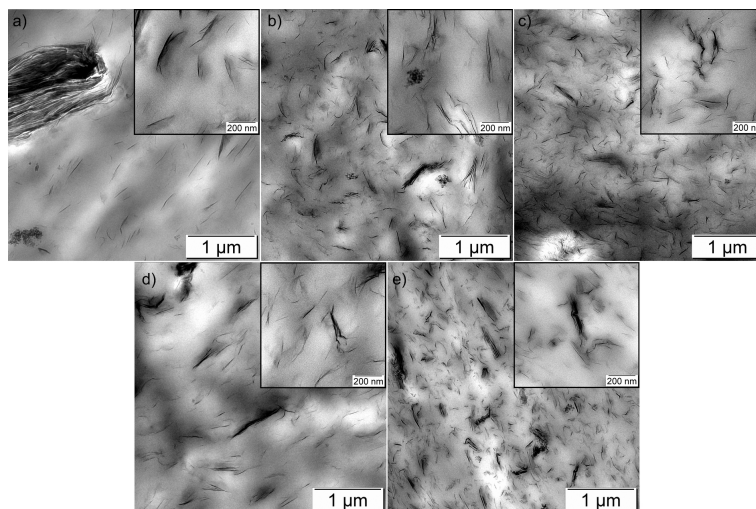


Figure 4.5: TEM pictures of PP-g-MA/C30B nanocomposites from classic PP-g-MA: NC1 (a), NC2 (b), NC3 (c), NC4 (d) and NC5 (e).

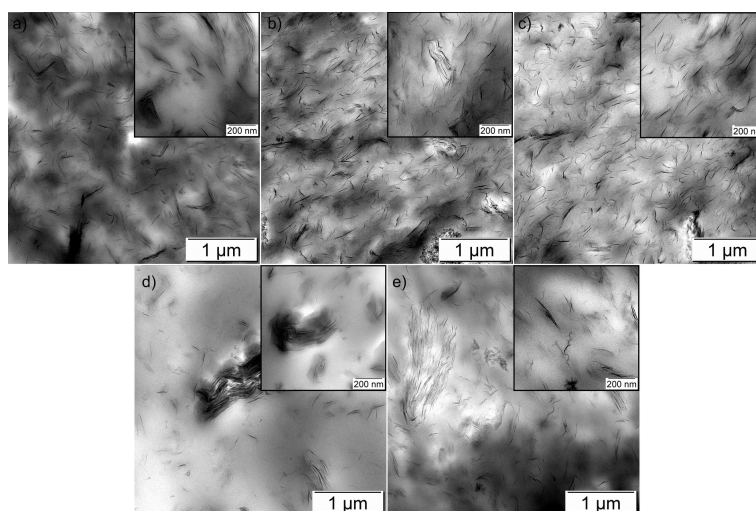


Figure 4.6: TEM pictures of PP-g-MA/C30B nanocomposites from NBS-mediated PP-g-MA: NC6 (a), NC7 (b), NC8 (c), NC9 (d) and NC10 (e).

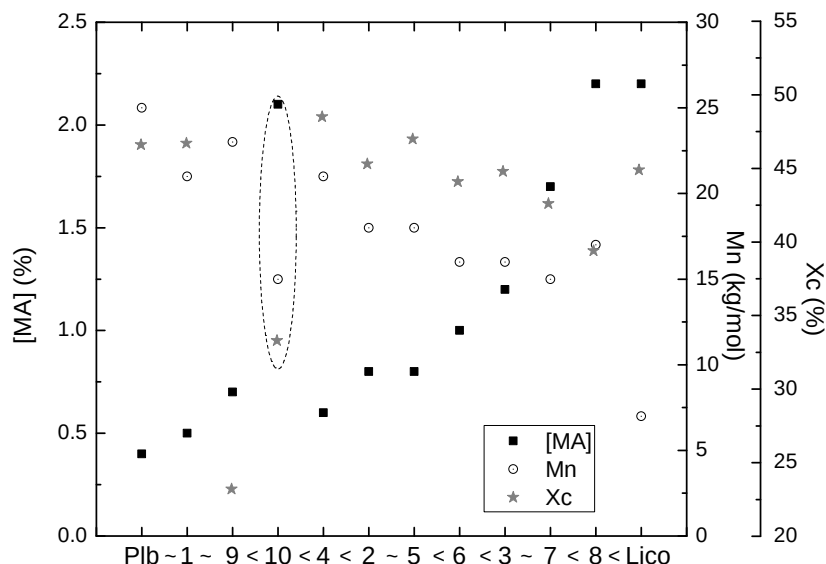


Figure 4.7: Evolution of the grafting level ([MA]), the number average molar mass (Mn) and of the crystallization degree (Xc) in function of PP-g-MAs ranked by increasing ability to disperse the organoclay.

a clay dispersion comparable to NCPlb and NC1.

In summary, the clay dispersion for the various PP-g-MA/C30B nanocomposites can be ranked as: NCPlb $\approx$ NC1 $\approx$ NC9 < NC10 < NC4 < NC2 $\approx$ NC5 < NC6 < NC3 $\approx$ NC7 < NC8 $\approx$ NCLico.

Influence of the PP-g-MA characteristics on the clay dispersion

Figure 4.7 shows the evolution of the grafting level ([MA]), the number average molar mass (Mn) and of the crystallization degree (Xc) in function PP-g-MAs ranked by their increasing of ability to disperse organoclay. The clay dispersion ability in nanocomposites prepared with commercial and classic PP-g-MAs (NCPlb $\approx$ NC1 < NC4 < NC5 $\approx$ NC2 < NC3 < NCLico) correlates with [MA], and Mn and Mw of the PP-g-MAs: the higher [MA] and the lower Mn are, the better the clay dispersion is. For nanocomposites based on NBS-mediated PP-g-MAs,

the increase of clay dispersion ($\text{NC9} < \text{NC10} < \text{NC6} < \text{NC7} < \text{NC8}$) no longer matches the increase of $[\text{MA}]$ and decrease of M_n and M_w . For example PP-g-MA 10 with high $[\text{MA}]$ and low M_n does not lead to a high clay delamination degree in NC10 (encircled in Figure 4.7). Nevertheless, discarding PP-g-MA 10, the global trend under Figure 4.7 is that the ability of a PP-g-MA to disperse organoclay raises when increasing its graft content and decreasing its molar mass. This trend is furthermore illustrated when comparing PP-g-MA 6 to 3 and 7 and PP-g-MA 2 to 8 showing that an increase of the PP-g-MA graft content independently of the other characteristics, raises the ability to disperse organoclay. Comparing PP-g-MA 10 to 8 and PP-g-MA 9 to 4, it can be noticed that a reduction of the PP-g-MA crystallinity independently of the other characteristics, strongly reduces the ability to disperse the clay. One possible explanation could be that NBS-mediated PP-g-MAs of low crystallinity have long chain branches which would limit the access of PP-g-MA inside the clay galleries due to steric hindrance. Henry et al. mentioned that long chain branches could be created upon the epimerization of PP [46]. When comparing Lico and PP-g-MA 8 having similar $[\text{MA}]$, it seems that there is no influence of the molar mass onto the clay dispersion. The higher mobility of low-molar mass Lico chains making easier their intercalation between the clay layers is probably counter-balanced by the higher mixing torque of PP-g-MA 8 favoring the clay dispersion.

As a result, in order to increase the clay dispersion, the use of PP-g-MAs of high graft content and unmodified crystallinity is recommended.

Thermal characterization

Clay platelets were shown having opposite effects on the crystallinity of polymers: [10, 21, 47–50] 1) a nucleation effect which facilitates and accelerates the crystallization process and 2) a steric effect of the exfoliated clay layers, which hinders polymer chain motions and retards the crystal growth. However, the presence of organoclay has no significant

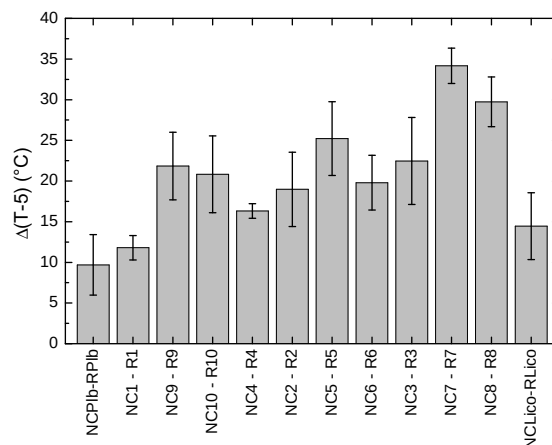


Figure 4.8: TGA results of PP-g-MA/C30B nanocomposites. $\Delta(T-5)$ is the difference between T-5 of nanocomposite and T-5 of reference. (samples in abscissa are ranked by increasing clay dispersion in the nanocomposite)

effect on the crystallinity of the synthesized PP-g-MA matrices.

Enhanced thermal stability is commonly observed when clay platelets are well-dispersed into the polymer matrix, as a result of hindered out-diffusion of the volatile decomposition products and also of char formation that acts as a physical barrier between the polymer and the oxidative medium[1, 18]. The T-5 difference ($\Delta(T-5)$) between references and nanocomposites are shown in Figure 4.8. As expected, the global trend is that $\Delta T-5$ raises with increasing clay dispersion; the greatest increase of thermal stability is measured for NC7.

4.3.4 PP/PP-g-MA blends

On the basis of the previous results, PP-g-MA 7 is selected as “optimum” PP-g-MA for the preparation of model PP-g-MA/organoclay nanocomposites. Indeed the latter reaches higher MA content than usual classic PP-g-MAs, while maintaining acceptable molar mass and unmodified crystallinity degree. For comparison PP-g-MA 2 is also con-

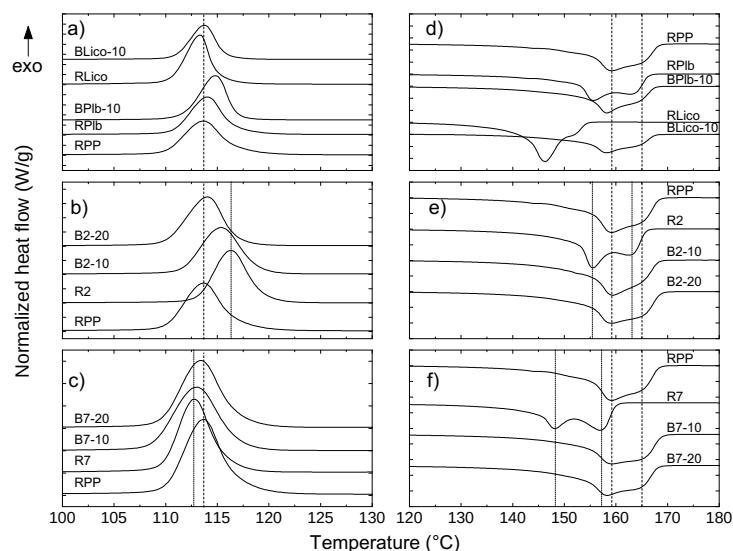


Figure 4.9: DSC curves of PP/PP-g-MA references and blends: Crystallization exotherms a), b) and c); melting endotherms d), e) and f).

sidered, which corresponds to a classic low-MA PP-g-MA.

The study of crystallization and melting of PP/PP-g-MA blends is performed in order to determine the (im)miscibility of PP-g-MAs with PP. Crystallization exotherms and melting endotherms of PP/PP-g-MA references and blends are displayed in Figure 4.9.

The melting curves of PP and PP-g-MAs show two endotherms, resulting from the melting of crystals of higher stability formed by re-crystallization of crystals initially obtained [51]. The crystallization exotherms and melting endotherms of BPlb-10 and BLico-10 are similar to PP suggesting that a clear phase-separation does not take place. Indeed, if Lico, which has high-MA content, was immiscible with PP, an additional melting peak, matching its own melting temperature (145 °C against 160–165 °C for PP) should be observed [16, 17, 52, 53].

PP/PP-g-MA 2 and PP/PP-g-MA 7 blends, whatever the weight fraction of PP-g-MA, show similar crystallization exotherms and melting endotherms to RPP, then suggesting that PP-g-MA 2 and 7 are mis-

cible and co-crystallize with PP. Moreover, contrary to B-elP20, TEM pictures of PP/PP-g-MA blends with PP-g-MA 2* or 7* (not shown), do not reveal any immiscibility between PP and PP-g-MA.

4.3.5 PP/Clay nanocomposites

A large-scale production of the selected home-made PP-g-MAs 2 and 7, labeled 2* and 7*, was performed on a twin-screw extruder. Characterizations of these samples (Table 4.4) show some [MA] reduction regarding the small-scale syntheses. This could be explained by the fact that only the screw speed and the throughput were adapted on the twin-screw extruder to reach approximatively the same residence time than on the single screw extruder.

PP/PP-g-MA/C30B nanocomposites were prepared by direct melt-blending with PP-g-MA 2* and 7* as compatibilizers. The resulting nanocomposites (NCP2* and NCP7*) are compared to a reference using commercial Plb as compatibilizer (NCPPlb). Figure 4.10 (XRD patterns of the PP-based nanocomposites) shows a shift of the C30B basal spacing to higher diffraction angles, meaning that at least part of the C30B silicate layers has collapsed. No intercalation or exfoliation sign is noticed on NCPPlb XRD pattern. NCP2* exhibits an additional shouldering around $2.5 - 3^\circ 2\theta$, attesting that part of the C30B layers has been intercalated. Although no intercalation sign is detected on NCP7* XRD pattern, a high diffraction intensity is observed toward low angles. This suggests that some clay layers are completely dispersed. TEM pictures of PP/PP-g-MA/C30B nanocomposites are presented in Figure 4.11. The clay dispersions of NCPPlb and NCP2* are very similar, showing a poor heterogeneous dispersion of very large aggregates with a few smaller clay stacks. The best clay dispersion is observed for NCP7* which exhibits a much more homogeneous dispersion with a mixed distribution of exfoliated clay layers and small clay aggregates.

The T-5 differences ($\Delta(T-5)$) between PP/PP-g-MA references (RPP2* and RPP7*) and PP/PP-g-MA/C30B nanocomposites (NCP2* and

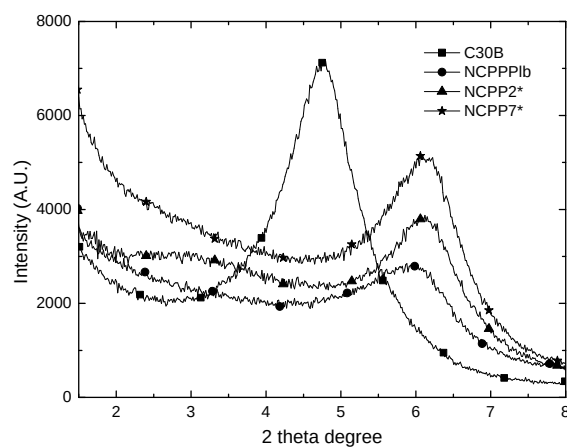


Figure 4.10: XRD patterns of PP/PP-g-MA/C30B nanocomposites.

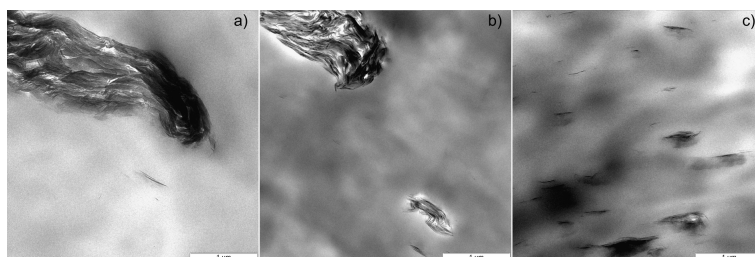


Figure 4.11: TEM pictures of PP/PP-g-MA/C30B nanocomposites: NCPPPlb (a), NCPP2* (b) and NCPP7* (c).

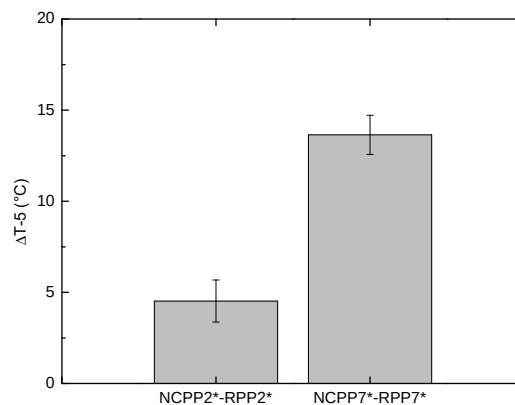


Figure 4.12: TGA results of PP/PP-g-MA/C30B nanocomposites.

NCPP7*) are shown in Figure 4.12. The increase of thermal stability is significantly more important with PP-g-MA 7* as compatibilizer than with PP-g-MA 2*. The higher degree of clay delamination reached using PP-g-MA 7* hinders more efficiently the out-diffusion of the volatile decomposition products.

4.4 Conclusions

The synthesis of polypropylene(PP)-graft-maleic anhydride (PP-g-MA) has been successfully tuned for the preparation of model PP-g-MA/clay nanocomposites and PP/clay nanocomposites. New PP-g-MAs were prepared by addition of N-bromosuccinimide (NBS) during the reactive extrusion process. The previously reported highly-grafted NBS-mediated PP-g-MAs prepared by using large amounts of NBS, had very high MA contents, high molar masses but no crystallinity, and were immiscible with PP. In this work, adapted amounts of NBS during the synthesis, led to new NBS-mediated PP-g-MAs having significantly higher graft contents than classic PP-g-MAs prepared without NBS but with acceptable molar masses and almost no drop of crystallinity. In

comparison, when synthesizing PP-g-MAs without NBS, high graft contents cannot be reached without recovering PP-g-MA waxes. The newly synthesized NBS-mediated and classic PP-g-MAs cover a wide range of graft content, molar masses and crystallinity.

All these PP-g-MAs have been used as matrices for the preparation of model PP-g-MA/clay nanocomposites in order to evaluate their ability to disperse the clay. As expected, PP-g-MAs possessing high graft content showed the best clay dispersion. However, we pointed out that PP-g-MAs presenting an important reduction of crystallinity display poor clay dispersion even when their $[MA]$ is high. Within the examined range of M_n and M_w , the PP-g-MAs molar masses had practically no influence on the clay dispersion. Nanocomposites prepared with NBS-mediated PP-g-MAs showed systematically a better clay dispersion than using the corresponding PP-g-MAs synthesized without NBS. In particular, PP-g-MA 7 was selected as “optimized” NBS-mediated PP-g-MA since the corresponding nanocomposite displayed the best improvement of thermal properties and one of the best clay dispersions.

PP/PP-g-MA blends have been prepared in order to evaluate the miscibility of PP-g-MAs with PP. All the tested PP-g-MAs appeared to be miscible with PP and able to co-crystallize with it.

Finally, the PP/organoclay nanocomposite prepared using the selected “optimized” NBS-mediated PP-g-MA, showed a better clay dispersion and thermal stability than the corresponding reference prepared with a classic PP-g-MA as compatibilizer. Hence this work demonstrates the advantage of using such new NBS-mediated PP-g-MAs as compatibilizers for the elaboration of PP/organoclay nanocomposites.

Acknowledgments

The authors thank La Région Wallonne and FRIA (Fonds pour la formation à la Recherche dans l’Industrie et dans l’Agriculture) for financial support. J. Marchand-Brynaert is Senior Research Associate of

the FRS-FNRS (Fonds National de la Recherche Scientifique, Belgium). P. Lipnik and P. Van Velthem are acknowledged for their contribution to the experimental work. Prof. J. Devaux and Prof C. Bailly (Université catholique de Louvain, UCL) are acknowledged for useful discussions and advices.

Appendix. Supporting information

Appendix 1: Short review on PP-g-MA used as matrix or compatibilizer in PP/clay nanocomposites.

This section refers to Table 4.1 in the main text.

Okada's team [8, 9, 28] firstly reported the elaboration of PP/organoclay nanocomposites by melt blending using PP-g-MA oligomers as compatibilizers. In a first study, Kato et al. prepared PP-g-MA oligomers/organoclay nanocomposites, comparing two PP-g-MA oligomers: PPMA-110TS and PPMA-1010 (Table 4.1) [28]. Only PPMA-1010, with highest acid value, was intercalated between organoclay layers. The authors also examined the effect of the PP-g-MA/clay weight ratio on the intercalation and showed a raise of the intercalation while increasing the PP-g-MA amount. Kawasumi et al. studied the miscibility effect of PP-g-MA oligomers on the dispersibility of organoclay in a PP matrix [8]. They used two PP-g-MA oligomers: PPMA-1001 and PPMA-1010 (Table 4.1). While no intercalation occurred with PP, both PP-g-MA oligomers were able to intercalate organoclay but it appeared that only PPMA-1001, with the lowest [acid], was miscible with PP. As a consequence, the best mechanical properties were obtained for the PP/organoclay nanocomposite using PPMA-1001. Hasegawa et al. reported the preparation of PP/clay nanocomposites by dilution of PP-g-MA oligomer/organoclay blends into PP [9]. PPMA-1010 was melt-blended with organoclay and an increase of the intercalation was observed when increasing the PP-g-MA/clay ratio. However no further increase of the clay basal spacing (XRD analysis) was observed when the PP-g-MA/organoclay blends

were diluted into PP, even if clay dispersion at the nanometer level was obtained at relatively high PP-g-MA content (22 wt.%). Since PPMA-1010 is immiscible with PP, the resulting material is rather a dispersion of the blend of organoclay intercalated by PP-g-MA, into the PP matrix. The authors recommend to use PP-g-MA with larger miscibility to PP in order to improve the dispersibility of the clay.

Reichter et al. studied the influence of the compatibilizer functionality on the formation of PP/organoclay nanocomposites [23]. Two PP-g-MA oligomers of high [MA] were used: E43 and HC5 (Table 4.1). Both PP-g-MAs gave similar increase of Young's modulus while PP/clay's yield stress increased more using HC5, with the highest [MA].

Koo et al. elaborated PP-g-MA/clay nanocomposites from two PP-g-MAs having the same MA content (approx. 2 wt.%) but with low and high molar masses (LMPP and HMPP, respectively, Table 4.1) [25]. The best mechanical and rheological properties were measured using the PP-g-MA of lowest Mw.

Bureau, Ton-That and Perrin-Sarazin [19–21] investigated PP/organoclay nanocomposites by comparing two PP-g-MAs with low and high [MA] respectively: PB3150 and E43 (Table 4.1). They reported that E43, with the lowest Mw, was more effective as coupling agent to disperse the clay layers but the Young's modulus of the nanocomposite was greater with PB3150 featuring the highest Mw. According to the authors, in a crystalline system, maximum PP/PP-g-MA compatibility can only be obtained if co-crystallization occurs. The critical PP chain length for the occurrence of such co-crystallization must correspond to a molar mass of 15 kg/mol. The AM content of PB3150 regarding E43 led to sufficient interactions with the clay platelets without reducing its compatibility with PP matrix, thus leading to a stronger interface and higher reinforcement.

Wang et al. prepared PP/organoclay nanocomposites by melt-blending with various PP-g-MAs [18]. They studied especially the influence of the MA content and the molar mass of PP-g-MAs on the clay exfolia-

tion and on PP/organoclay nanocomposites properties. Four PP-g-MAs were compared: PB3150, PB3200, PB3000 and E43 (Table 4.1). All PP-g-MAs led to similar degrees of clay dispersion beyond a PP-g-MA/clay ratio of 3:1, excepted E43 due to its low Mn leading to poor mixing torque and consequently to a poor clay dispersion. In PP/clay nanocomposites, well-dispersed clay layers, mainly exfoliated, were observed with PB3150 and PB3000 while poorly dispersed aggregates were seen with E43. Despite the wide range of MA content employed, no immiscibility drawback between PP-g-MA and PP matrix was noticed. Discarding E43, rheological results demonstrated that PP-g-MA of low molar mass and high MA content led to better interaction with the clay. In following work, Wang et al. studied the effect of the same four PP-g-MAs on rheology of PP/organoclay nanocomposites [22]. E43 showed the least enhancement on the composite complex viscosity while PB3000 exhibited the greatest enhancement among other Polybond PP-g-MAs.

Lopez-Quintanilla et al. investigated the effect of using two PP-g-MA with different low-[MA]: PB3001 and PB3200 (Table 4.1) on the preparation and mechanical properties of PP/organoclay nanocomposites [27]. They reported that intercalation and mechanical properties were enhanced by increasing the MA content of the PP-g-MA allowing a better interfacial adhesion between clay and matrix.

Dubnikova et al. studied the influence of four PP-g-MA (PO2011, PB3002, PB3150 and AR504, Table 4.1) on the properties of PP/organoclay nanocomposites [24]. In PP-g-MA/organoclay nanocomposites the intercalation capability of the PP-g-MA increased up to [MA] = 1.3 wt.% and then decreased a little bit when [MA] reaches 4 wt.% (AR504). According to the authors, the decrease of clay interlayer spacing with AR504, in comparison with PB3150, is related to a difficulty of the polymer chains to diffuse into the clay galleries due to the stronger polymer/clay interactions. In PP/organoclay nanocomposites, the clay intercalation and dispersion raised while increasing [MA]. The best clay intercalation and dispersion in PP/organoclay nanocomposites, was ob-

tained using AR504, with the highest MA content. However, the latter has limited miscibility with PP and worsens crystalline structure of the polymer matrix whereas PP-g-MAs with lower MA content have weaker intercalation ability but well co-crystallize with PP. The higher mechanical reinforcement was obtained using PB3002, which has, according to the authors, the most optimal parameters (high Mw and [MA] = 0.6 wt.%) for intercalation capability, polymer/clay adhesion and miscibility with polymer matrix.

Eteläaho et al. examined two types of PP-g-MA (AR504 and TPPP-2112, Table 4.1) for the elaboration of PP/organoclay nanocomposites [26]. The clay dispersion was the best using AR504, featuring the lowest Mn and the highest [MA], than using TPPP2112 where a greater amount of exfoliated clay layers were visible. However, in comparison with PP/organoclay composites without PP-g-MA, the use of AR504 impaired the mechanical performances while the use of TPPP2112 exhibited almost no enhancement of the mechanical properties in comparison with the PP matrix. According to the authors, TPPP2112 would probably need more time and higher shear forces to function effectively.

Appendix 2: Definitions of active oxygen and active bromine.

Active oxygen ($O\bullet$) is defined as the amount of oxygen in the free radical initiator that will react to give free radicals capable of causing removal of the hydrogen radical from a tertiary carbon of the polymer [54]. $O\bullet$ is the maximum concentration of active oxygen-based free radicals produced by the organic peroxide (Equation 4.1). m_{perox} is peroxide mass, 15.9994 is atomic mass of oxygen, n_O is the number of active oxygen atom in the peroxide molecule, M_{perox} is peroxide molar mass ($M_{DHP} = 290.44 \text{ g/mol}$) and m_{PP} is PP mass.

$$O\bullet = \frac{m_{perox} \cdot 15.9994 \cdot n_O}{M_{perox} \cdot m_{PP}} \cdot 100 \quad (4.1)$$

Using supported DHP as peroxide, the mass of supported DHP

peroxide ($m_{DHBP_{sup.}}$) can be calculated using Equation 4.2. The number 2 takes into account that DHBP is 50 wt% blend with silica and the number 22.068 is the weight percentage of oxygen in DHBP.

$$m_{DHBP_{sup.}} = \frac{O \bullet \cdot 2 \cdot m_{PP}}{22.068} \quad (4.2)$$

Active bromine ($Br\bullet$) is defined as the proportion of the total bromine content of the bromine compound, it is the maximum concentration of bromine free radicals that could be produced (Equation 4.3). m_{R-Br} is bromine compound mass, 79.9 is atomic mass of bromine, n_{Br} is number of bromine atom in the bromine compound and M_{R-Br} is molar mass of bromine compound ($M_{NBS} = 177.98 \text{ g/mol}$).

$$Br\bullet = \frac{m_{R-Br} \cdot 79.9 \cdot n_{Br}}{M_{R-Br} \cdot m_{PP}} \cdot 100 \quad (4.3)$$

Using NBS as bromine compound, the mass of NBS (m_{NBS}) can be calculated using Equation 4.4. The number 44.89 is the weight percentage of bromine in NBS.

$$m_{NBS} = \frac{Br \bullet \cdot m_{PP}}{44.89} \quad (4.4)$$

Appendix 3: Infrared spectroscopy (FTIR) - Titration calibration curve

FTIR spectra were recorded on a Nicolet Nexus 870 FTIR spectrometer on compression-molded films in transmission mode by cumulating 16 scans at a resolution of 4 cm^{-1} over a spectral range from 4000 to 400 cm^{-1} . Films were obtained by compression-molding of washed PP-g-MA. The spectra of PP-g-MA were normalized by setting the peak height of the 973 cm^{-1} absorption band to an absorbance of 1. This band, which is assigned to isotactic helices, is usually used as an internal reference for comparison of films of different thickness [29].

PP-g-MAs often present on their infrared spectra both anhydride and acid bands due to hydrolysis of the anhydride functions into diacid

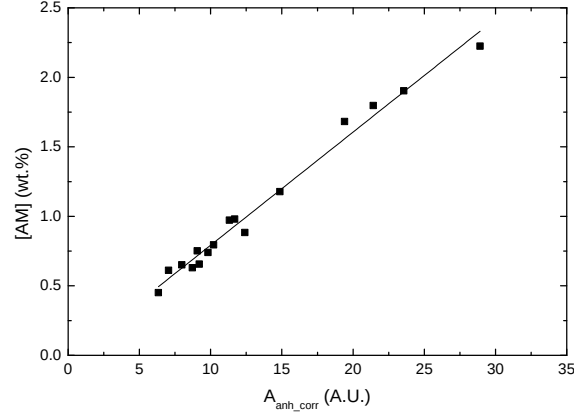


Figure 4.13: Titration-Infrared spectroscopy correlation for the determination of the grafted maleic anhydride content.

ones [31]. In order to take also into account the anhydride open into diacid, the anhydride and acid band area (A_{anh} , A_{acid} , respectively) are both measured. A corrected anhydride band (A_{anh_corr}) is calculated using Equation 4.5. The factor 1.3 which divides the A_{acid} corresponds to the ratio of the molar extinction coefficients of anhydride on acid bands and was previously determined by Rousseaux et al. [31]. The corrected anhydride band area is the area of the anhydride band that would have been measured if no anhydride functions was hydrolyzed into acid.

$$A_{anh_corr} = A_{anh} - (A_{acid}/1.3) \quad (4.5)$$

Figure 4.13 depicts the [AM] measured by titration for a series of PP-g-MA as a function of their A_{anh_corr} measured by FTIR. A linear regression, using Equation 4.6, can be used to estimate the [AM] of a washed PP-g-MA through their infrared analysis.

$$[AM] = (0.0814 \cdot A_{anh_corr}) - 0.0219 \quad (4.6)$$

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Chapter 5

Carboxylate Clays for Polypropylene/Clay Nanocomposites

Le deuxième acteur que nous avons étudié est l'argile. Nous avons mis en évidence la possibilité de modifier simplement l'argile native par des sels d'acides carboxyliques, de préférence de l'acétate de sodium. Ces nouvelles argiles carboxylées, peu coûteuses et thermiquement stables, sont intéressantes pour la fabrication de nanocomposites. Elles peuvent remplacer les argiles organomodifiées traditionnelles.

Carboxylate clays: a model study for polypropylene/clay nanocomposites.

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Polym. Degrad. Stab. 2010, 95(7), p. 1194-1204

Work presented at the 25th Annual Meeting of the Polymer Processing Society (PPS-25), 2009 (Goa, India) and at the 26th Annual Meeting of the Polymer Processing Society (PPS-26), 2010 (Banff, Canada).

Abstract

Sodium-montmorillonite was intercalated by carboxylate salts to prepare carboxylate clays. The intercalation of sodium acetate doubles the clay basal spacing and no degradation of the carboxylate clay is noticed in the extrusion temperature range. These carboxylate clays were used to synthesize polypropylene-graft-maleic anhydride (PP-g-MA)/clay nanocomposites. Nanocomposites were also produced by a one-pot process using *in situ* prepared carboxylate clay. The carboxylate salts within the clay layers, are used to partially neutralize the maleic anhydride groups of the PP-g-MA matrix, *in situ* during the melt compounding. The ionic groups of the partially neutralized polymer offer favorable interactions with the clay, hence reinforcing the interfacial junction between the polymer and the clay and improving the composite properties. The use of carboxylate clay clearly improves the clay dispersion into the PP-g-MA matrix and rises the nanocomposite thermal and rheological properties.

5.1 Introduction

Polymer/clay nanocomposites investigation received a considerable scientific and technological interest during the last decades. The rea-

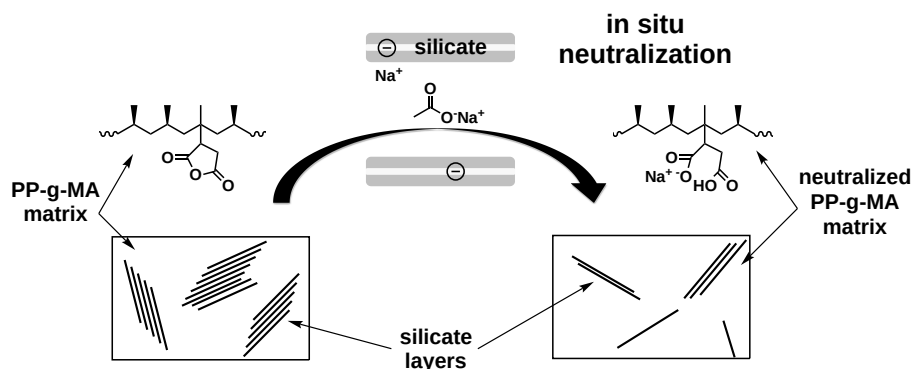


Figure 5.1: Graphical Abstract

sons are the easy availability of clay, the wide knowledge concerning the clay intercalation chemistry and last but not least, the enhancements of the polymer matrix properties that could be obtained with just a few percents of filler; e.g. higher mechanical and barrier properties, flame retardant behavior while the material transparency is preserved [1–4]. The most commonly employed clay for the preparation of polymer nanocomposites is montmorillonite. Sodium-montmorillonite is a layered aluminosilicate mineral with sodium counterions present between the clay layers. The silicate layers of montmorillonite feature typical sizes in the order of one nanometer thick to hundreds nanometer long. Their high length/thick ratio usually around 800, offers large surface area for polymer/filler interactions.

For obtaining polymer/clay nanocomposites, the clay layers which are naturally stacked into aggregates of several microns, need to be separated and dispersed into the polymer matrix. The more separated and dispersed the clay layers are, the higher the surface area for polymer/filler interactions and the better the overall properties enhancements are.

The most usual way to produce polymer/clay nanocomposites is by melt-blending in an extruder where the clay layers are separated and dispersed into the molten polymer. The melt-blending synthesis is in-

expensive, environmentally-friendly and straightforward [4–6]. Nanocomposites made by melt-blending are synthesized almost exclusively from organoclays due to the lack of compatibility between most polymers and clays [1, 2, 5, 7]. In organoclays, organic cationic surfactants, mostly alkylammoniums, replace sodium interlayer cations of the untreated clay [7]. The introduction of surfactants increases the interlayer spacing and lowers the clay surface energy which facilitates separation and dispersion of the clay layers into the polymer matrix.

The main problem of producing polymer/clay nanocomposites concerns the thermal stability of the surfactant in the organoclay. The interlayer alkylammonium surfactants often decompose at extrusion temperatures leading to a collapse of the silicate layers and limiting the composite properties [8–11]. Moreover, aforementioned decomposition products impart undesirable color, odor and taste to the composite [12]. Efforts have been made to synthesize more thermally stable organoclays using other cationic surfactants. For example pyridinium and quinolinium [13], imidazolium [14], phosphonium [15] and stibonium [16] 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.

Polypropylene (PP) is one of the most used matrix in polymer/clay nanocomposites due to its very large commercial importance [17]. PP/clay nanocomposites are usually prepared by melt-blending, using compatibilizers like PP-graft-maleic anhydride (PP-g-MA) and organoclays [18–20]. Compatibilizers are required due to the huge difference of polarity between the polyolefin matrix and the clay. PP-g-MA allows wetting of the clay surface by hydrogen-bond interactions between the anhydride functions (in fact, the acid functions are always present due to hydrolysis under the usual storage conditions [21]) and the oxygen atoms at the surface of the silicate layers. Also hydrogen-bond interactions could occur between the clay hydroxyl groups and the PP-g-MA carbonyl functions.

The present paper reports the synthesis of carboxylate clays by in-

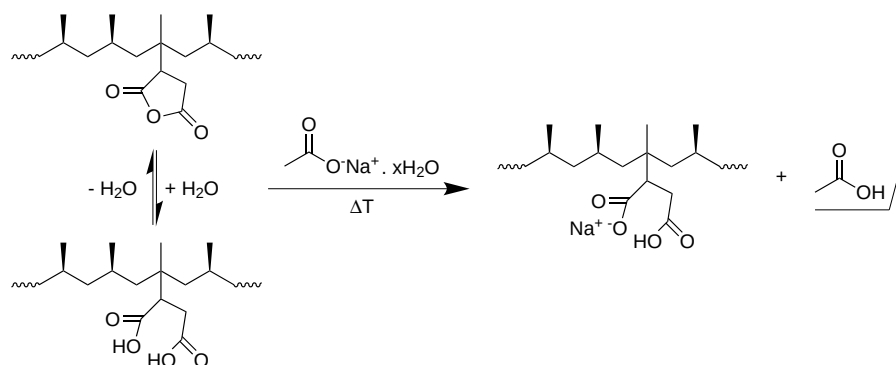


Figure 5.2: Neutralization of PP-g-MA into ionomer by sodium acetate.

tercalating carboxylate salts inside sodium-montmorillonite interlayers. These carboxylate clays are promising materials for the production of polypropylene/clay nanocomposites. The carboxylate salts, intercalated within the clay layers, are used to neutralize PP-g-MA anhydride/acid groups *in situ*, as shown in Figure 5.2.

In the case of sodium acetate, PP-g-MA is partially neutralized into an ionomer form; only one of the two carboxylic acid functions of the anhydride can be neutralized [21]. The ionic groups of the ionomer compatibilizer offer favorable interactions with the clay [22]. The use of partially neutralized PP-g-MA ionomers as compatibilizers will offer both hydrogen-bond and ionic interactions to link the compatibilizer to the silicate layers, hence reinforcing the interfacial junction between the polymer and the clay and improving the composite properties.

The originality in this work is the preparation of innovative carboxylate clays and the study of their structural and thermal properties. Two preparation methods of carboxylate clays are compared. Different carboxylate salts at different concentrations were intercalated into the silicate layers. The clay basal spacing was measured by X-ray diffraction and the clay thermal stability by thermogravimetric analysis. The interactions between the clay and the carboxylate salts were investigated by infrared spectroscopy. Finally, PP-g-MA/clay nanocomposites

were synthesized from a carboxylate clay and compared with a reference nanocomposite based on untreated clay. Nanocomposites were also produced from untreated clay by synthesizing *in situ* the carboxylate clay. The clay dispersion was examined by X-ray diffraction and transmission electron microscopy. The neutralization of PP-g-MA was examined by infrared spectroscopy. The nanocomposites were characterized by thermal and mechanical analyses.

5.2 Experimental

5.2.1 Materials

Sodium-montmorillonite (Cloisite Na⁺, labeled CNa) was purchased from Southern Clay Product. Before use, Cloisite Na⁺ was dried (dCNa) at 100 °C under vacuum. Anhydrous sodium acetate (NaAc), trihydrate sodium acetate (NaAc · 3 H₂O), sodium propionate (NaPro) and sodium butyrate (NaBut), all of analysis grade, were purchased from Sigma-Aldrich. Methanol (MeOH) of analysis grade, was purchased from Fluka. Water was standard laboratory demineralized water. Commercial PP-g-MA Polybond 3200 (1 wt.% of maleic anhydride, labeled Plb) was purchased from Chemtura. Commercial organoclay Nanofil 948 (labeled NF948) used for comparison in thermogravimetric analysis, was purchased from Süd Chemie.

5.2.2 Sample preparation

Carboxylate clays synthesis. Carboxylate salt amounts are added in equivalent (equiv.) quantities in respect to the cation exchange capacity of CNa (0.92 meq./g). Two preparation methods are applied and compared.

Water-method: The standard method to prepare alkylammonium clays [23] was adapted to prepare carboxylate clays. 1 g of untreated clay (CNa) is dispersed into 100 ml of water at 80 °C and 5 equiv. of NaAc (0.114 g) are solubilized into 100 ml of water at 80 °C. The NaAc

solution is added to the clay dispersion and stirred for 4 h. The product is filtered, dried at 100 °C under vacuum and ground (sample W5 in Table 5.1).

MeOH-method: 5 g of dCNa and the carboxylate salt (NaAc, NaPro or NaBut) are dispersed both into 80 ml of methanol at room temperature. The suspension is vigorously stirred until complete evaporation of the solvent at room temperature. The residue is dried at 100 °C under vacuum and ground using a ball mill and passed through various sieves until the maximum particle size was less than 100 μm . The compositions of the carboxylate clays prepared by the MeOH-method are reported in Table 5.1 (samples C1 to C9).

Table 5.1: Composition of the carboxylate clays prepared using the Water-method (W5) and the MeOH-method (C0 to C9).

Sample code	Sample name	Salt	Salt amount (equiv.)
W5	Water-(CNa-5NaAc)	NaAc	5
C0	MeOH-(dCNa)	-	0
C1	MeOH-(dCNa-1NaAc)	NaAc	1
C2	MeOH-(dCNa-2NaAc)	NaAc	2
C3	MeOH-(dCNa-3NaAc)	NaAc	3
C4	MeOH-(dCNa-4NaAc)	NaAc	4
C5	MeOH-(dCNa-5NaAc)	NaAc	5
C6	MeOH-(dCNa-3NaPro)	NaPro	3
C7	MeOH-(dCNa-5NaPro)	NaPro	5
C8	MeOH-(dCNa-3NaBut)	NaBut	3
C9	MeOH-(dCNa-5NaBut)	NaBut	5

Nanocomposites synthesis. References and nanocomposites samples were prepared in a DSM Xplore 15 ml microcompounder with Polybond 3200 (Plb) as matrix. The samples were extruded at a screw speed of 200 RPM at 200 °C during 2 minutes. The clay proportion is 5 wt.% of inorganic content for nanocomposites while reference samples do not contain clay. Two preparation methods are used: (1) The sequential process (SP) in which carboxylate clay is melt-blended within PP-g-MA

matrix (reference R0 and nanocomposites NC-SP0 and NC-SP1 in Table 5.2); (2) The one-pot process (OP) in which dCNa and carboxylate salt are melt-blended within PP-g-MA matrix (references R0, R-OP1 and R-OP2 and nanocomposites NC-OP0, NC-OP1 and NC-OP2 in Table 5.2).

5.2.3 Characterizations

X-ray diffraction (XRD). The interlayer spacing of the different clays and nanocomposites was measured by XRD on a Bruker D8 Advance diffractometer using $\text{CuK}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) at 40 kV and 30 mA. Clays XRD patterns are recorded on powder and nanocomposites XRD patterns on compression-molded films pressed at 200 °C during maximum 5 seconds.

Thermogravimetric analysis (TGA). The thermal stability of the different clays and nanocomposites was studied by TGA. The analyses were performed on a Mettler Toledo TGA/SDTA 851^e using a heating rate of 20 °C/min under air or nitrogen atmosphere (100 ml/min) from 25 to 1000 °C. TGA results on nanocomposites are presented as temperatures at 5% (T-5), 10% (T-10) and 50% (T-50) weight loss under air atmosphere and each value is the average of three experiments. T-5, T-10 and T-50 are usually considered as the initial decomposition temperature, the onset and the midpoint of the degradation, respectively.

Fourier Transform Infrared (FTIR) spectroscopy. FTIR spectra were obtained on a Nicolet Nexus 870 FTIR spectrometer equipped with an Continuum microscope in attenuated total reflectance (ATR) mode using a slide-on accessory with a Si crystal. The spectra for clay samples were recorded by cumulating 128 scans at a resolution of 4 cm^{-1} over a spectral range from 4000 to 650 cm^{-1} in ATR mode. The spectra for nanocomposite samples were recorded in transmission mode on compression-molded films by cumulating 16 scans at a resolution of 4 cm^{-1} over a spectral range from 4000 to 400 cm^{-1} . The nanocompo-

Table 5.2: Composition of the nanocomposites (NC) and references (R) prepared by sequential (SP) and one-pot processes (OP).

Sample code	Sample name	Clay	Clay amount (wt.% inorg.)	Salt	Salt amount (equiv.)
R0	P1b	-	0	-	0
NC-SP0	P1b-5[MeOH-(dCNa)]	C0	5	-	0
NC-SP1	P1b-5[MeOH-(dCNa-5NaAc)]	C5	5	-	0
R-OP1	P1b-5NaAc	-	0	NaAc	5
R-OP2	P1b-5NaAc · 3H ₂ O	-	0	NaAc · 3H ₂ O	5
NC-OP0	P1b-5dCNa	dCNa	5	-	0
NC-OP1	P1b-5dCNa-5NaAc	dCNa	5	NaAc	5
NC-OP2	P1b-5dCNa-5NaAc · 3H ₂ O	dCNa	5	NaAc · 3H ₂ O	5

site spectra were normalized by setting the peak height of the 2723 cm^{-1} absorption band (characteristic C-H stretching of PP) to an absorbance of 1.

Transmission electron microscopy (TEM). Clay dispersion of nanocomposite samples was examined on TEM pictures. Samples were ultra-microtomed at ambient temperature with a Reichert Microtome and collected on a copper grid. TEM pictures were recorded with a LEO 922 microscope operating at 200 kV.

Rheology. Rheological measurements were carried out in an oscillatory mode on a Bohlin Gemini II rheometer equipped with a parallel plate geometry using 25 mm diameter plates. Frequency sweep tests were performed under nitrogen atmosphere, at $180\text{ }^{\circ}\text{C}$ with strain of 10% on compression-molded samples of about 1 mm in thickness. Experimental conditions were determined to work within the linear viscoelastic regime.

5.3 Results and discussion

5.3.1 Carboxylate clays

Before synthesis, untreated clay (CNa) is dried (dCNa) at $100\text{ }^{\circ}\text{C}$ under vacuum in order to remove the interlayer water. The clay basal spacing (001) shifts from 1.24 nm ($7.1\text{ }^{\circ}2\theta$) to 0.97 nm ($9.1\text{ }^{\circ}2\theta$) (Figure 5.3). The basal spacing measured for CNa corresponds to the presence of one layer of water in the clay interlayer and to a completely dehydrated sodium montmorillonite for dCNa [24, 25].

By using the water-method (the standard method in the case of alkylammonium clays) to prepare a carboxylate clay (sample W5 in Table 5.1), no clay intercalation was noticed (results not shown). Preparation of carboxylate clay using methanol (MeOH) instead of water is then considered. A series of carboxylate clays with increasing amounts of NaAc (in equiv.) has been synthesized (samples C1 to C5 in Table 5.1). Sample C0 was prepared following the MeOH-method without addition of

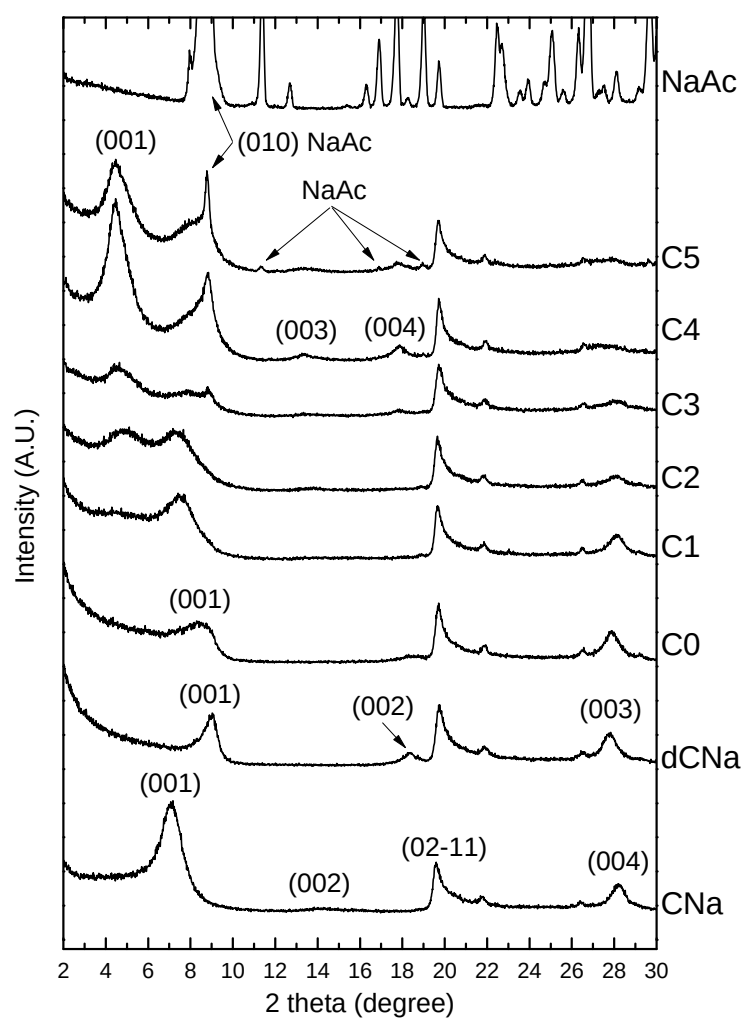


Figure 5.3: CNa, dried CNa (dCNa), MeOH treated dCNa (C0), carboxylate clays (C1 to C5) and NaAc XRD patterns (the patterns are vertically shifted).

carboxylate salt. XRD was used to monitor the clay basal spacing of carboxylate clays (Figure 5.3). The slight shift to lower angle and widening of basal spacing in the C0 pattern probably results from a less ordered stacking of the silicates layers caused by the treatment the clay undergoes during the MeOH-method (drying, grinding). At one equivalent of NaAc (C1), the clay basal spacing (001) shifts from 0.97 nm ($9.1^\circ 2\theta$) in the dCNa to 1.2 nm ($7.45^\circ 2\theta$) and a shoulder appears between 4 and $5^\circ 2\theta$. This basal spacing increase to 1.2 nm results from water uptake. The shoulder at 2.0 nm ($4.4^\circ 2\theta$) is the basal spacing (001) of the carboxylate clay. NaAc intercalates the untreated clay by doubling the basal spacing. When increasing the amount of NaAc, the (001) reflexion at $7.45^\circ 2\theta$ progressively disappears while the basal spacing of the carboxylate clay continues to rise. At 3 equiv. of NaAc (C3), the basal reflexion at $7.45^\circ 2\theta$ has almost disappeared and the (010) reflexion of NaAc becomes detectable at $8.8^\circ 2\theta$. The appearance of the NaAc (010) reflexion corresponds to a part of NaAc not intercalated assuming that crystalline NaAc is excluded of the silicate layers. At 4 equiv. of NaAc (C4), the basal spacing (001) of the carboxylate clay is well defined and others (00L) reflexions are visible: (002) around $8-9^\circ 2\theta$ but superposed with (010) NaAc reflexion, (003) at $13.4^\circ 2\theta$ and (004) at $17.8^\circ 2\theta$. The (010) reflexion of NaAc is also well defined at 4 equiv. of NaAc. At 5 equiv. of NaAc (C5), other reflexions belonging to NaAc become visible at 11.3 , 16.9 and $19.0^\circ 2\theta$. Supposing that a part of the introduced NaAc is not intercalated, 5 equiv. of introduced NaAc should assure a sufficient amount of NaAc to completely intercalate the clay. Attempts to wash carboxylate clays with MeOH in order to remove excess NaAc failed; both intercalated and excess NaAc were eliminated and untreated clay was recovered.

The use of MeOH instead of water plays a key role in this synthesis. MeOH solubilizes the carboxylate salt and swells the clay [26]. Clay contains both Brönsted acid sites (in the interlayers) and Lewis acid sites (at the edges) [27]. The clay acidity is largely influenced by the

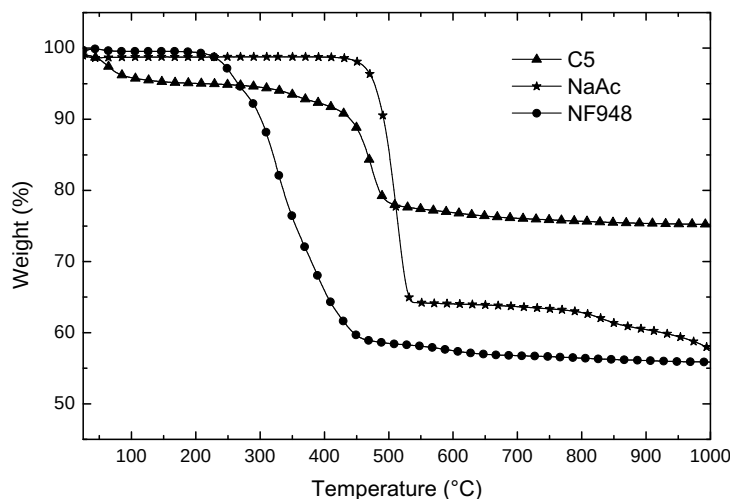


Figure 5.4: C5 carboxylate clay, anhydrous sodium acetate (NaAc) and alkylammonium-clay (NF948) TGA patterns (under nitrogen atmosphere).

quantity of intercalated water. The Brönsted acidity derives from the dissociation of water directly coordinated to interlayer cations [27, 28]. When interlayer water is removed until only one layer of water remains, the Brönsted acidity becomes very strong. When continuing the removal of water, e.g. by heating, the Brönsted acidity decreases and the Lewis acidic character increases [27, 29]. The masked Lewis acidity of the hydrated clay explains the water-method failure. In the case of the MeOH-method, the water is driven out due to drying and displacing by methanol in large excess. In the clay interlayers, the Lewis acidity increases and becomes more important than the Brönsted one. This increase of the Lewis acidic character explains the easy intercalation of sodium acetate.

The thermal stability of C5 carboxylate clay has been examined under nitrogen atmosphere and compared to pure NaAc and to an usual alkylammonium clay NF948 (Figure 5.4). The early weight loss (around 100 °C) on the C5 carboxylate clay profile, corresponds to water des-

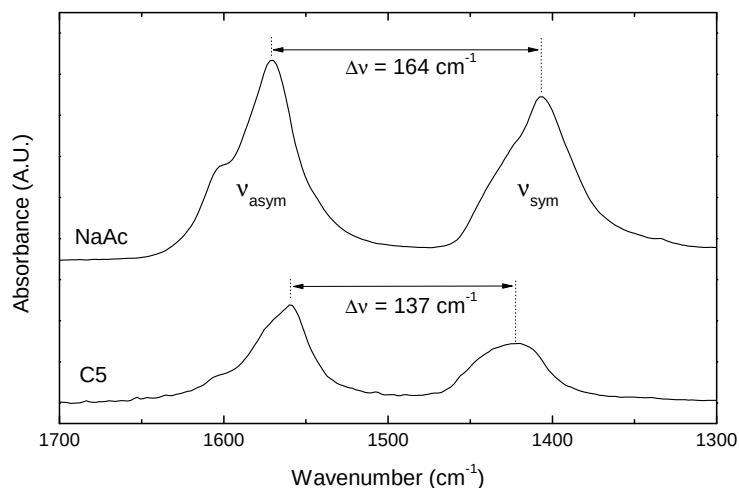


Figure 5.5: C5 carboxylate clay and NaAc FTIR patterns (the patterns are vertically shifted).

orption. The carboxylate clay remains very polar and quickly uptakes ambient water. The NaAc intercalated inside the silicate layer begins to degrade to a lower temperature (300–400 °C) than pure NaAc (450–550 °C). This phenomenon is probably due to a catalytic effect of the Lewis or Brönsted sites as it was observed for alkylammonium when intercalated inside the clay [8]. The 19% loss occurring on the C5 profile between 300 to 600 °C precisely corresponds to 5 equiv. of acetate (organic content of NaAc). The thermal degradation of C5 carboxylate clay is strongly delayed in comparison to NF948 alkylammonium clay. Carboxylate clay appears more thermally stable than alkylammonium clay and can thus be used in the extrusion temperature range (between 200 to 300 °C) without thermal degradation drawback.

The interaction between the clay and the carboxylate salt has been investigated by FTIR. Figure 5.5 shows infrared spectra enlargement of the respective carbonyl region for C5 carboxylate clay and for NaAc. The carbonyl asymmetric stretching (ν_{asym}) of the carboxylate function is around 1560–1570 cm^{-1} and the symmetric one (ν_{sym}) around

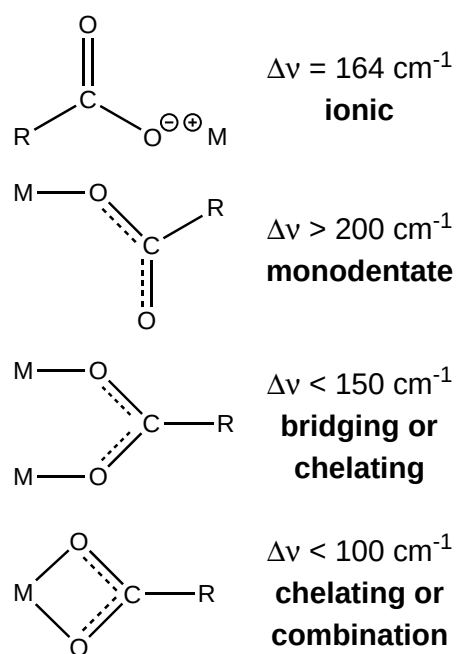


Figure 5.6: Carboxylate shift values to determine the carboxylate coordination, according to Deacon and Phillips [30].

1400–1420 cm^{-1} . Comparatively to NaAc, the carboxylate clay shows a decrease of the asymmetric stretching and an increase of the symmetric one. The separation between the symmetric and asymmetric stretchings, called the carboxylate shift ($\Delta\nu$) is 164 cm^{-1} for NaAc and 137 cm^{-1} for C5 carboxylate clay. Deacon and Philips have suggested an empirical rule derived from observations on crystalline metal acetate complexes, to determine the carboxylate coordination type [30]. This rule, that has been further confirmed by ab initio calculations [31], correlates the "carboxylate shift" ($\Delta\nu$) to the type of coordination of the carboxylate group, as summarized in Figure 5.6. For C5 sample, the $\Delta\nu$ value suggests a bridging- or chelating-type ($\Delta\nu < 150 \text{ cm}^{-1}$). Since sodium cations are in excess, because coming at once from the sodium acetate and from the clay interlayer, bridging-type coordination is more probable (Figure 5.7). The decrease of $\Delta\nu$ proves that intercalated NaAc interacts well with the clay layers. C1 to C5 $\Delta\nu$ measurements are presented in Table 5.3. The $\Delta\nu$ value increases with the amount of NaAc. At low NaAc amount, all the salt could be completely intercalated inside (see above XRD results) the clay galleries and could interact with the silicate layers. When increasing the salt amount, a crystalline NaAc fraction appears. Assuming that the crystalline NaAc is excluded from the silicate galleries, it would less interact with the silicate layers than the intercalated NaAc. The presence of crystalline NaAc most probably explains the rise of the carboxylate shift with the increase of NaAc amount.

Intercalation of other carboxylate salts with increasing alkyl chain length was considered in view to increase the interlayer spacing. Different carboxylate clays were prepared using 3 and 5 equiv. of sodium propionate (NaPro, samples C6 and C7) and sodium butyrate (NaBut, samples C8 and C9). The clay basal spacing (001) shifts from 0.97 nm to 1.70 nm ($5.2^\circ 2\theta$) when modified with NaPro (see Figure 5.14 in supporting information). At 3 equiv. of NaPro, the carboxylate clay (001) basal reflexion is well defined and the main reflexion of NaPro at $7.8^\circ 2\theta$

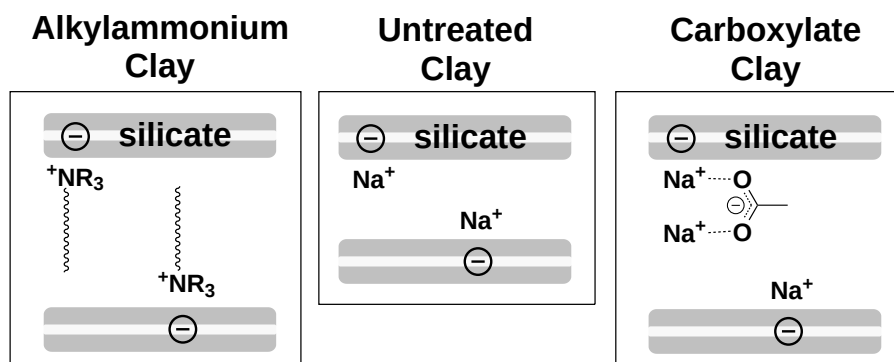


Figure 5.7: Proposed structure of carboxylate clay, comparatively to untreated clay and alkylammonium clay.

Table 5.3: Carboxylate shift measurements

Samples	$\Delta\nu$ (cm^{-1})
NaAc	164
C1	125
C2	125
C3	128
C4	131
C5	137
NaPro	142
C6	134
C7	136
NaBut	146
C8	140
C9	140

is visible but more important with 5 equiv. of salt. The clay basal spacing of the carboxylate clay modified with NaBut is superposed to the main reflexion of the NaBut around $6^\circ 2\theta$ (see Figure 5.15 in supporting information). Using the (003) reflexion of the carboxylate clay at $18^\circ 2\theta$, it is possible to estimate the basal spacing (001) of the clay modified with NaBut around 1.47 nm ($6.0^\circ 2\theta$). The interlayer spacing varies inversely to the alkyl chain length. This could be due to the less solubility of NaPro and NaBut in methanol than NaAc. The Deacon and Phillips' rule established on acetate complexes has been also applied to the coordination of other simple carboxylate ions [30]. C6 to C9 $\Delta\nu$ measurements are reported in Table 5.3 (C7 and C9 FTIR spectra are shown in Figures 5.16 and 5.17 of supporting information). The $\Delta\nu$ decrease of the intercalated NaPro or NaBut suggests also a bridging coordination. However, the shift of $\Delta\nu$ is less important for the intercalated NaPro and NaBut than for NaAc indicating that the interactions with the clay layers are lower than with NaAc.

5.3.2 PP-g-MA/carboxylate clay nanocomposites

PP-g-MA/carboxylate clay nanocomposites were prepared by two different methods: (1) the sequential process in which preformed carboxylate clay is melt-blended within PP-g-MA matrix; (2) the one-pot process in which carboxylate clay is synthesized *in situ* during melt-blending of the nanocomposite. Table 5.2 presents the composition of references and nanocomposites prepared by both processes.

The nanocomposites were characterized by XRD to follow the evolution of the clay basal spacing. Figure 5.8 shows the XRD patterns of nanocomposites prepared by the sequential process (a) and by the one-pot process (b). The NC-SP0 basal spacing centered at 1.23 nm ($7.2^\circ 2\theta$) probably results from water uptake into the silicate layers. No further intercalation of the C5 carboxylate (basal spacing at 2.01 nm, $4.4^\circ 2\theta$) is observed on the NC-SP1 XRD pattern but the presence of the peak at 1.23 nm ($7.2^\circ 2\theta$) is attributed to some loss of intercalated NaAc,

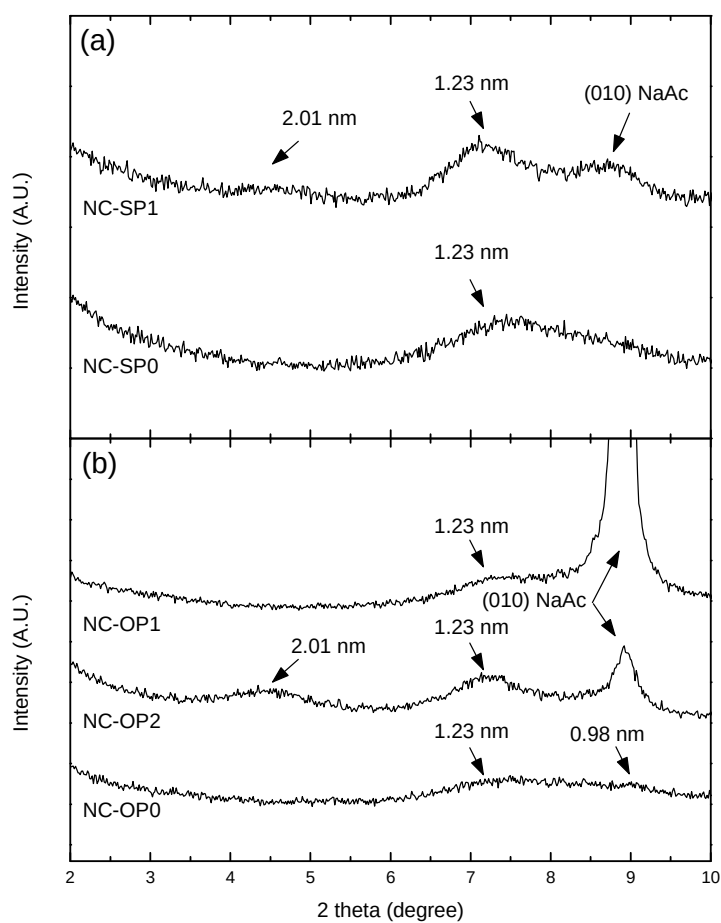


Figure 5.8: XRD patterns of (a) nanocomposites prepared by the sequential process (b) nanocomposites prepared by the one-pot process (the intensity scales are not the same for the two charts and the patterns are vertically shifted).

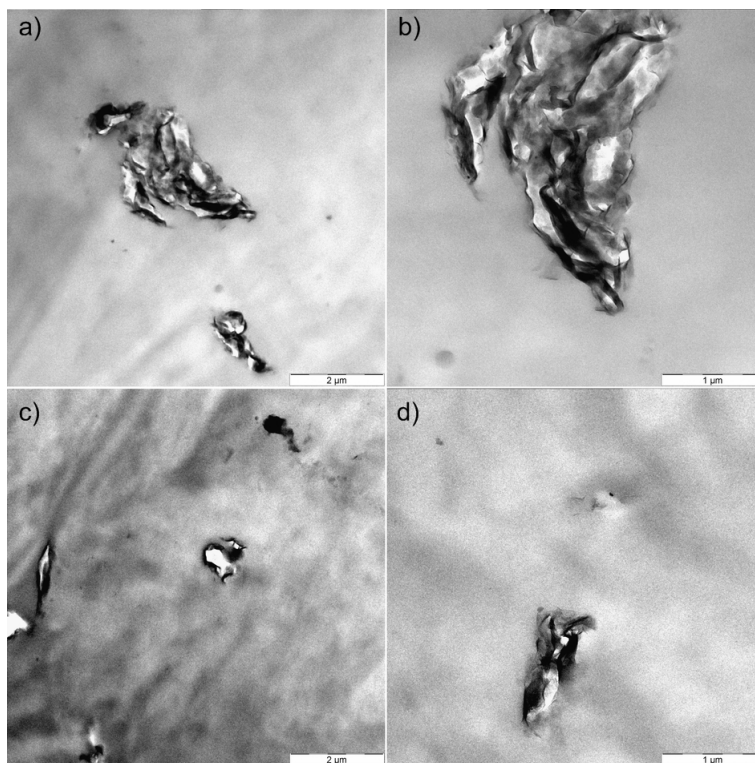


Figure 5.9: TEM pictures of NC-SP0 (a,b) and of NC-SP1 (c,d) at a magnification of 2,300 and 5,000 respectively.

probably due to PP-g-MA neutralization. In NC-OP0, the basal spacing at 0.98 nm ($9.0^\circ 2\theta$) corresponds to dried untreated clay (value similar to dCNa) and the one at 1.23 nm ($7.2^\circ 2\theta$) results from water uptake into the silicate layers like for NC-SP0 (value similar to CNa). NaAc does not intercalate dCNa in NC-OP1 while NaAc $\cdot$ 3H₂O does well in NC-OP2 (basal spacing at 2.01 nm, $4.4^\circ 2\theta$). Moreover, the large (010) NaAc reflexion in NC-OP1 suggests that all the NaAc is crystalline and excluded out of the silicate layers. NaAc $\cdot$ 3H₂O intercalation into dCNa is attributed to its low melting temperature. Anhydrous sodium acetate melts at 325 °C while the trihydrate salt melts at 58 °C, liberating its crystallization water which is evaporated under the process temperature.

TEM analyses were performed to examine the clay dispersion in



Figure 5.10: TEM pictures of NC-OP0 (a,b), NC-OP1 (c,d) and NC-OP2 (e,f) at a magnification of 2,300 and 5,000 respectively. Exfoliated clay layers are indicated with arrows.

the nanocomposites. Figures 5.9 and 5.10 show TEM pictures of nanocomposites prepared by the sequential process and by the one-pot process, respectively. NC-SP0 exhibits, as expected, only large clay aggregates of several microns. By using C5 carboxylate clay in NC-SP1 preparation, clay aggregates are broken into smaller ones and the overall clay dispersion is slightly better than in NC-SP0. The clay dispersion of NC-OP0 and NC-OP1 are similar to those of NC-SP0 and NC-SP1, respectively. The best clay dispersion is observed for NC-OP2 which shows a mixed morphology of small clay stacks with individual clay platelets homogeneously distributed into the Plb matrix. The clay dispersion is clearly improved when carboxylate clay is *in situ* prepared using $\text{NaAc} \cdot 3\text{H}_2\text{O}$.

PP-g-MA neutralization by sodium acetate was monitored by FTIR. Figure 5.11(a) shows FTIR spectra in the carbonyl region of reference and nanocomposites prepared by the sequential process and Figures 5.11(b) and (c) of references and nanocomposites prepared by the one-pot process, respectively. Three main absorption bands can be observed in the $1500\text{--}1800\text{ cm}^{-1}$ carbonyl region : (1) the maleic anhydride band (carbonyl symmetric stretching) around 1780 cm^{-1} ; (2) the carboxylic acid band (carbonyl stretching) around 1715 cm^{-1} and (3) the carboxylate band (carbonyl asymmetric stretching) around 1565 cm^{-1} . Plb matrix (R0) shows a slightly more intense acid band than the anhydride one. This is explained by the hydrophilicity of PP-g-MA anhydride moieties which absorb ambient moisture and form carboxylic diacid functions (see Figure 5.2). For PP-g-MA stored in air atmosphere at room temperature, all the anhydride functions are usually transformed into diacid functions. Due to the process high temperature, part of the carboxylic diacid functions closed to reform anhydride, liberating water which is evaporated. NC-SP0 shows a more intense anhydride band and a smaller acid band than in R0 indicating that more diacid functions cyclized into anhydride functions in the presence of clay. This phenomenon could be explained by the trapping of liberated water by the hydrophilic

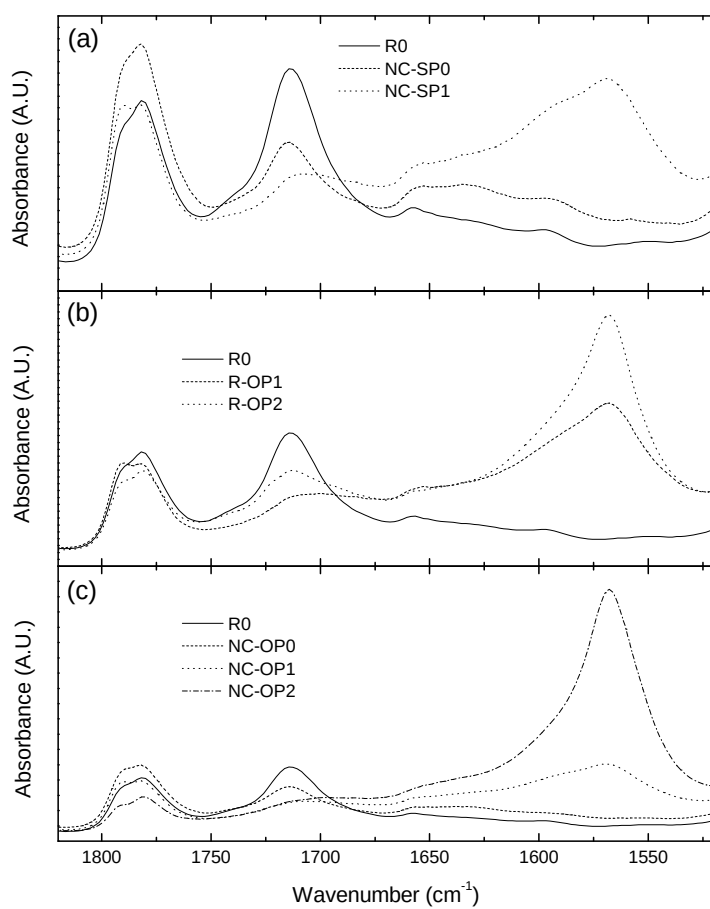


Figure 5.11: FTIR spectra of (a) reference and nanocomposites prepared by the sequential process, (b) references prepared by the one-pot process and (c) nanocomposites prepared by the one-pot process.

dried untreated clay. More water should be eliminated out of the matrix in the presence of dCNa, thus displacing the reaction toward more anhydride formation. The decrease of NC-SP1 anhydride and acid bands results from a partial neutralization of PP-g-MA by NaAc. NC-SP1 carboxylate band arises from the carboxylate product of the neutralization but also from the excess of NaAc. The larger decrease of the anhydride band and the more intense carboxylate band in R-OP2 than in R-OP1 indicate a greater efficiency of $\text{NaAc} \cdot 3\text{H}_2\text{O}$ to neutralize PP-g-MA than NaAc. Indeed, the neutralization reaction requires water to ionize the base [21]. NC-OP0 and NC-OP1 spectra are similar to those of NC-SP0 and R-OP1 respectively. NC-OP1 shows however a slightly smaller anhydride band and a slightly more intense carboxylate band, indicating that R-OP1 is more neutralized than NC-OP1. This phenomenon can be due to the partial trapping by untreated clay of the liberated water (from diacid closing into anhydride) which is required to ionize NaAc for the neutralization reaction. NC-OP2 presents a larger decrease of both anhydride and acid bands and a more intense carboxylate band regarding R-OP2. Hence, the clay amplifies the PP-g-MA neutralization by $\text{NaAc} \cdot 3\text{H}_2\text{O}$ while it is not the case when using NaAc.

When untreated clay is dispersed into Plb matrix, like in NC-SP0 and NC-OP0, only hydrogen bond interactions (via anhydride and acid functions) are available to link PP-g-MA to the clay. Interestingly, when both sodium acetate and clay are melt-blended into Plb, like in NC-SP1, NC-OP1 and NC-OP2, both hydrogen-bond and ionic interactions (via carboxylate functions) become available. As ionic interactions are stronger than hydrogen-bonds, the interfacial junction between polymer and clay should be reinforced and a better clay dispersion is expected. The weak neutralization of PP-g-MA by NaAc explains the slightly better clay dispersion in NC-SP1 and NC-OP1. In NC-OP2, as the neutralization is amplified, more ionic interactions are created to link the polymer to the clay. This is probably the reason of the better clay dispersion obtained for NC-OP2 regarding the other composites.

For NC-OP2, three possible reaction pathways can be suggested: (a) first neutralization of PP-g-MA by $\text{NaAc} \cdot 3\text{H}_2\text{O}$ followed by intercalation of the resulting PP-g-MA ionomer into the untreated clay galleries; (b) first intercalation of $\text{NaAc} \cdot 3\text{H}_2\text{O}$ into the clay galleries followed by *in situ* neutralization of PP-g-MA into the carboxylate clay galleries or at the external surface of the carboxylate clay stacks; (c) simultaneous intercalation of the clay and neutralization of PP-g-MA, both by $\text{NaAc} \cdot 3\text{H}_2\text{O}$. The measurement of the same basal spacing at 2 nm for NC-OP2 prepared by the one-pot process using $\text{NaAc} \cdot 3\text{H}_2\text{O}$ and C5 carboxylate clay excludes the proposition (a). Indeed, higher basal spacing should be observed if PP-g-MA ionomer had intercalated the untreated clay. The propositions (b) and (c) cannot be discriminated. As no further intercalation of carboxylate clay is noticed while individual clay platelets are observed for NC-OP2, one can suppose that clay dispersion/exfoliation is achieved by a peeling mechanism due to hydrogen-bond and stronger ionic interactions available between the clay and the compatibilizer.

5.3.3 Thermal and rheological properties of PP-g-MA/carboxylate clay nanocomposites

The thermal stability study of the nanocomposites gives indirect information on the state of dispersion of the clay. Higher thermal stability is commonly observed when clay platelets are well-dispersed into the polymer matrix due to the diffusion lengthening of gas molecules resulting from matrix degradation. Figure 5.12 presents the TGA results for references and nanocomposites prepared by the sequential and one-pot processes. T-5 and T-10 of NC-SP0 and NC-SP1 are not significantly different from R0. Their respective T-50 is about 10 °C higher for NC-SP0 and 25 °C higher for NC-SP1 than for R0. This suggests a slightly better clay dispersion with clay intercalated by NaAc than with untreated clay. The addition to Plb of NaAc (R-OP1), $\text{NaAc} \cdot 3\text{H}_2\text{O}$ (R-OP2) or dCNa (NC-OP0) does not change significantly T-5 and T-10. The higher T-50

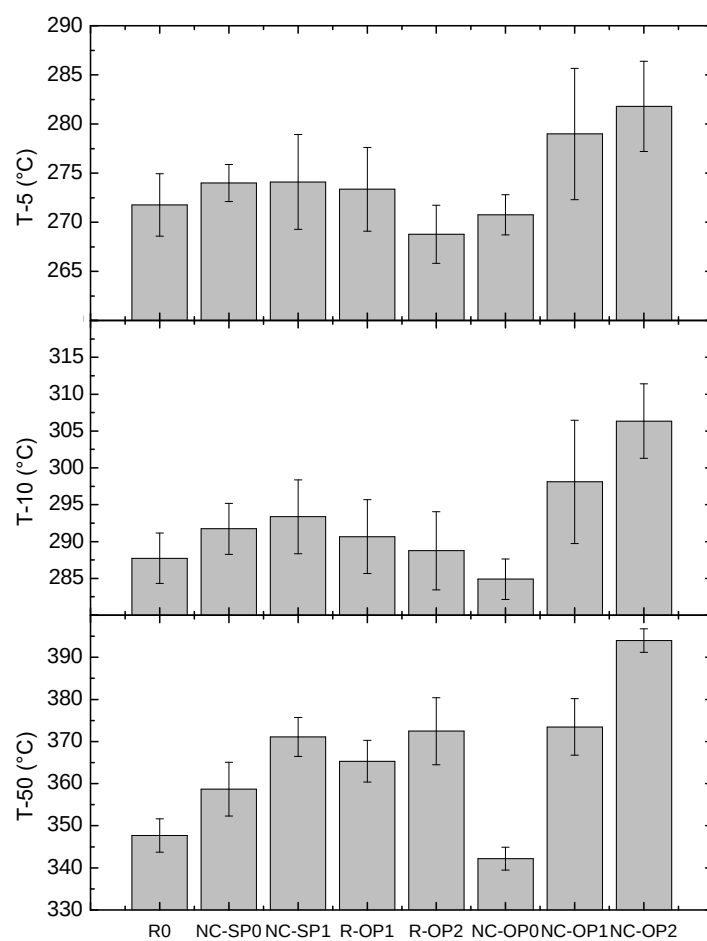


Figure 5.12: Temperatures at 5% (T-5), 10% (T-10) and 50% (T-50) weight loss under air atmosphere for references and nanocomposites prepared by the sequential process and the one-pot process.

of R-OP1 and R-OP2 regarding R0 indicates an increase of the thermal stability of these PP-g-MA ionomers. This phenomenon results from ionic aggregation of the carboxylate moieties which holds together polymer segments resulting from matrix degradation [21]. T-5, T-10 and T-50 of NC-OP1 and NC-OP2 are significantly higher than the corresponding R-OP1, R-OP2 and NC-OP0 samples. The simultaneous addition of dCNa and sodium acetate (anhydrous or trihydrate) improves the thermal stability of the composite. NC-OP2 however exhibits the best thermal stability over the all range of temperatures, suggesting a better clay dispersion than in the other compounds. Two phenomena could explain the higher thermal stability of NC-OP2: (a) the neutralization amplification leading to more ionic aggregation; (b) a better clay dispersion than in other composites. It is difficult to discriminate the two phenomena for NC-OP2. However, the higher thermal stability of NC-OP1 than R-OP1 is not correlated to its degree of neutralization since R-OP1 is more neutralized than NC-OP1 and consequently, the higher thermal stability of NC-OP1 must be attributed to a better clay dispersion. Moreover, there is no doubt about the experimental evidences of a better clay dispersion in NC-OP2.

Rheological characterization is the appropriate method to reveal the dispersion state of the global materials. Indeed, melt flow behavior is quite sensitive to the structure, particle size, shape and surface properties of a dispersed phase [32, 33]. When a percolating mesoscopic filler network is obtained, a significant increase of the elastic modulus at low frequencies is observed and an elastic modulus plateau most often appears. Figure 5.13(a) shows the elastic modulus curves of reference and nanocomposites prepared by the sequential process and Figure 5.13(b) of references and nanocomposites prepared by the one-pot process. The small elastic modulus increase of NC-SP0 regarding R0 can be attributed to a slight reinforcement due to the presence of clay linked to PP-g-MA by hydrogen-bonds. Two phenomena could explain the further elastic modulus increase of NC-SP1 regarding NC-SP0 and R0: (a)

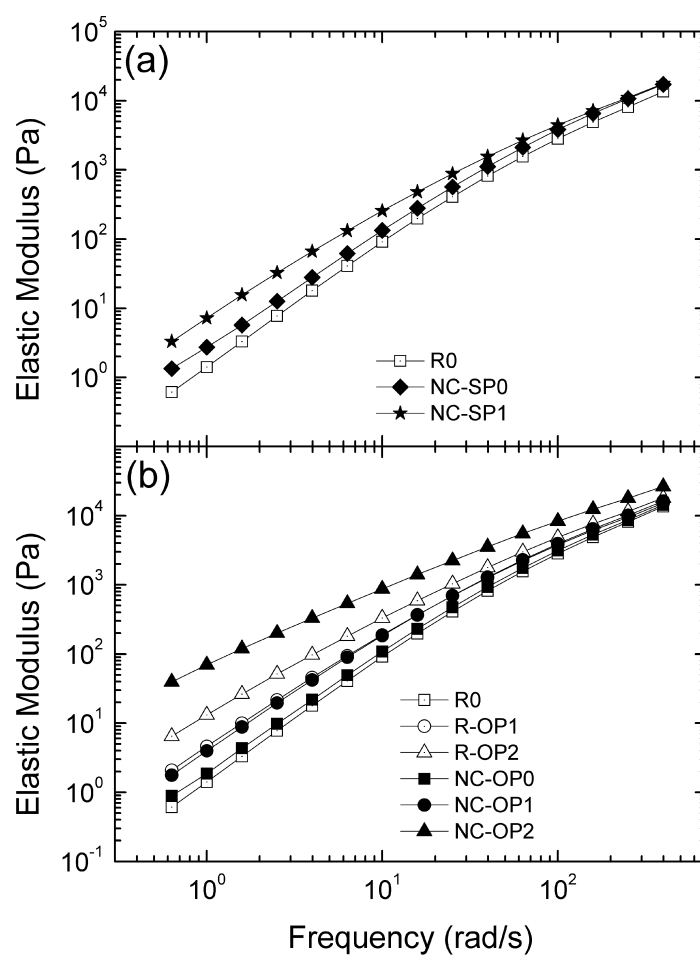


Figure 5.13: Elastic modulus at 180 °C as a function of the frequency for (a) reference and nanocomposites prepared by the sequential process and (b) references and nanocomposites prepared by the one-pot process.

a matrix reinforcement due to the clay linked to polymer matrix by both hydrogen-bond and stronger ionic interactions; (b) a matrix reinforcement by ionic aggregation of the carboxylate moieties. Ionic aggregation in NC-SP1 made by the sequential process is supposed to be negligible since the amount of NaAc not intercalated into C5 carboxylate clay is weak. Consequently, the NC-SP1 elastic modulus increase is attributed to the carboxylate clay and both hydrogen-bond and ionic interactions. The increase of R-OP1 and R-OP2 elastic modulus only results from ionic aggregation of the carboxylate moieties. Ionic aggregation is a thermoreversible crosslinking that limits the polymer chains to flow. As $\text{NaAc} \cdot 3\text{H}_2\text{O}$ is more efficient than NaAc to neutralize PP-g-MA, the extent of ionic aggregation is greater and the elastic modulus is raised further. The lower elastic modulus increase of NC-OP0 regarding R0 comparatively to NC-SP0 and R0 could be due to a less ordered stacking of the MeOH-treated silicate layers (clay C0) which would slightly facilitate the clay dispersion. As the elastic moduli of R-OP1 and NC-OP1 are similar, the NC-OP1 elastic modulus increase comparing to Plb (R0) is only attributed to ionic aggregation resulting from NaAc addition. The situation is quite different for NC-OP2 where its elastic modulus is raised of about one decade in comparison to R-OP2 and of about two decades regarding R0. The two previous phenomena could be again invoked. Contrarily to NC-SP1, the ionic aggregation cannot be neglected as all the reactants are added simultaneously. Moreover in NC-OP2, the clay was shown amplifying the neutralization of PP-g-MA by $\text{NaAc} \cdot 3\text{H}_2\text{O}$. Nevertheless, since we have established the *in situ* synthesis of carboxylate clay and the better clay dispersion in NC-OP2, it is difficult to discriminate between the two possible causes of matrix reinforcement. The NC-OP2 elastic modulus increase is however markedly superior to the sum of the increases of elastic modulus for NC-OP0 and R-OP2. This improvement clearly results from a synergy effect of the simultaneous addition of clay and $\text{NaAc} \cdot 3\text{H}_2\text{O}$ to the Plb matrix.

5.4 Conclusions

Carboxylate clays were successfully synthesized and characterized. The synthesis method involves the use of methanol as solvent at room temperature. Three carboxylate salts were intercalated inside the untreated clay galleries: sodium acetate, sodium propionate and sodium butyrate. The higher basal spacing is obtained when intercalating sodium acetate into the silicate layers. The carboxylate clay modified with sodium acetate is more thermally stable than a classical alkylammonium clay and does not degrade at extrusion temperature (200-300 °C). Infrared investigations on carboxylate clays show changes in carboxylate coordination modes confirming interactions between the intercalated carboxylate salts and the clay layers (see Figure 5.7).

The carboxylate clay prepared with sodium acetate is the best candidate to examine the feasibility of using such a clay to prepare polymer/clay nanocomposites via a sequential process. In this model study, PP-g-MA (the usual compatibilizer for PP/alkylammonium nanocomposites) was considered. PP-g-MA/carboxylate clay nanocomposites were also prepared by an one-pot process, by synthesizing *in situ* the carboxylate clay during the melt-blending of PP-g-MA and clay. Nanocomposites prepared by this one-pot process, by the combined addition of clay and trihydrate sodium acetate, exhibit the best clay dispersion and the best thermal and rheological properties. All the characterizations converge to show a strong synergy effect of the clay and the trihydrate sodium acetate.

When synthesizing the carboxylate clay, it was chosen to use anhydrous sodium acetate and dried untreated clay as reagents, especially because the initially tested, so-called “water-method” failed. Anhydrous sodium acetate, like its trihydrate form, is completely soluble in methanol. The intercalation of sodium acetate into the clay galleries by the so-called “methanol-method” was explained by the strong Lewis acidic character exhibited by the dehydrated clay. The situation is different when synthesizing nanocomposites via the one-pot process which

requires the use of trihydrate sodium acetate instead of the anhydrous form. Only the trihydrate sodium acetate can melt at the process temperature. Hence, a good mixing of all the components is only possible with trihydrate sodium acetate. Moreover, water is required to ionize sodium acetate for allowing the neutralization of PP-g-MA.

For the nanocomposites synthesized by the sequential process, sodium acetate is first intercalated into the clay galleries. Then, intercalated sodium acetate neutralizes the anhydride/acid functions of PP-g-MA during the nanocomposite compounding. The water required for base ionization probably comes from PP-g-MA itself when closing the diacid functions into anhydride due to the process high temperature. For the nanocomposites prepared by the one-pot process using $\text{NaAc} \cdot 3\text{H}_2\text{O}$, two possible reaction routes cannot be discriminated: (1) the initial intercalation of sodium acetate into clay galleries followed by *in situ* neutralization of PP-g-MA by the carboxylate clay; (2) simultaneous intercalation of the clay and neutralization of PP-g-MA by the hydrated sodium acetate. This work paves the route towards the use of untreated montmorillonite for the preparation of PP/clay nanocomposites. Works are in progress considering home-made PP-g-MAs as compatibilizer and PPs.

Acknowledgments

The authors thank La Région Wallonne and FRiA (Fonds pour la formation à la Recherche dans l'Industrie et dans l'Agriculture) for financial support. J. Marchand-Brynaert is Senior Research Associate of the FRS-FNRS (Fonds National de la Recherche Scientifique, Belgium). Prof. Ph. Dubois (Université de Mons, UMH), Prof. J. Devaux (Université catholique de Louvain, UCL) and Prof C. Bailly (UCL) are acknowledged for useful discussions and advices and P. Lipnik for her contribution to the experimental work.

Supporting information

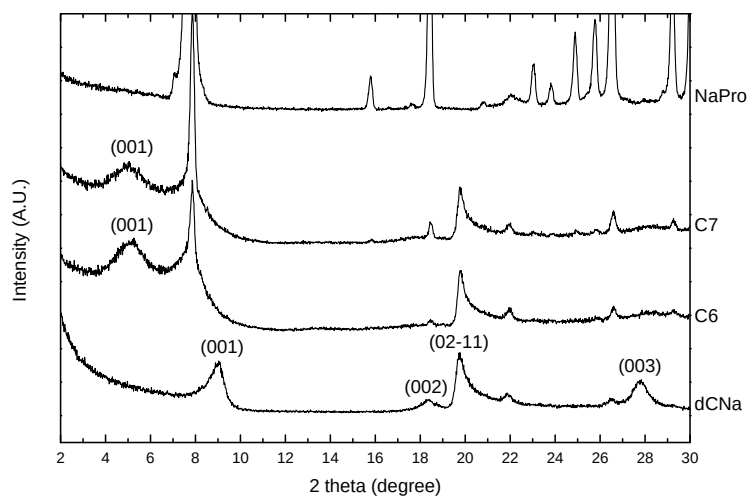


Figure 5.14: C6 and C7 carboxylate clays XRD patterns (the patterns are vertically shifted).

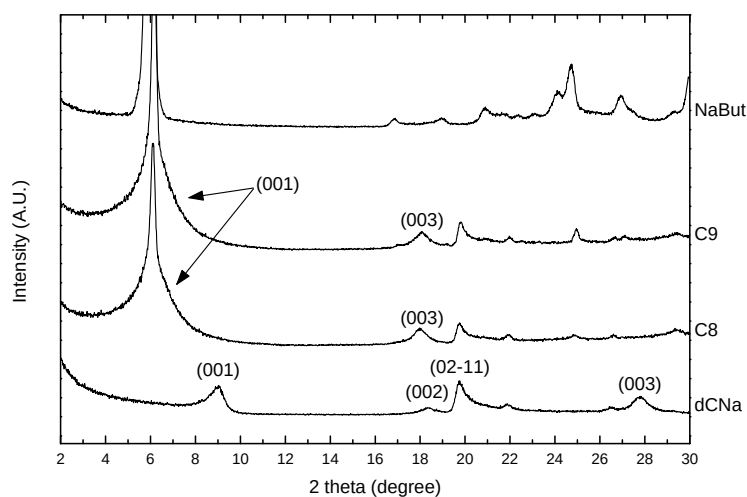


Figure 5.15: C8 and C9 carboxylate clays XRD patterns (the patterns are vertically shifted).

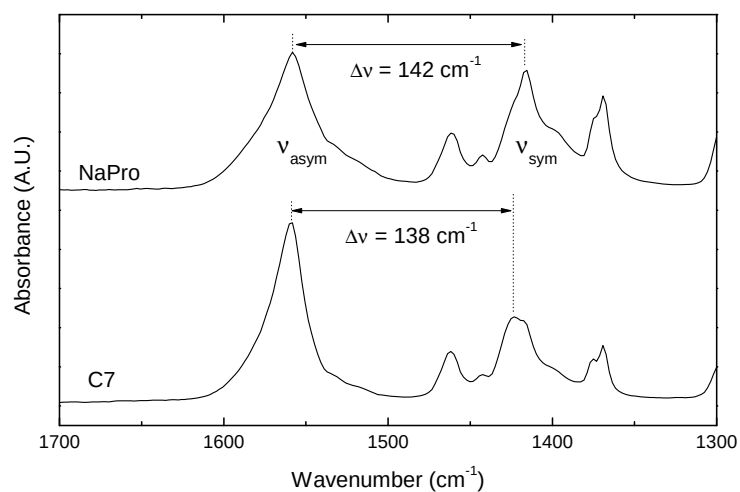


Figure 5.16: C6 and C7 carboxylate clays FTIR patterns (the patterns are vertically shifted).

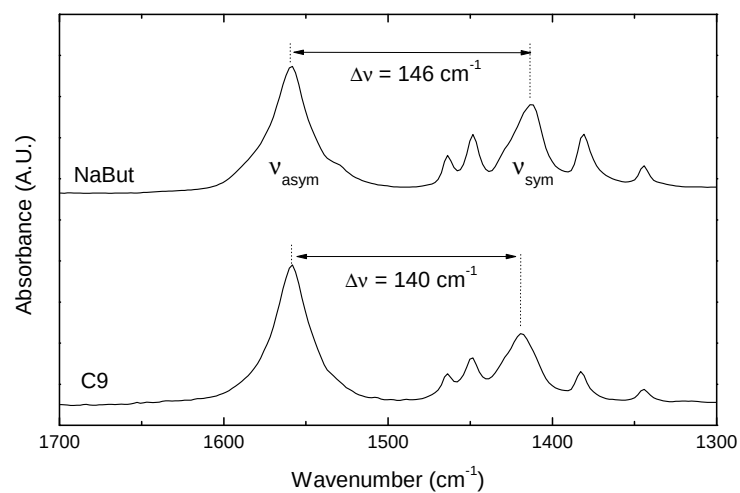


Figure 5.17: C8 and C9 carboxylate clays FTIR patterns (the patterns are vertically shifted).

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Chapter 6

Process Improvements in Polypropylene/Clay Nanocomposites Elaboration

Dans cette partie du travail, nous avons tenté d'améliorer le procédé classique d'extrusion pour synthétiser des nanocomposites. Un système d'injection d'eau dans le mélange fondu, connu dans le cas des polyamides, a été transposé au cas du polypropylène. La dispersion de l'argile et les propriétés des nanocomposites sont significativement augmentées lorsque l'on applique ce procédé au mélange PP-g-MA/argile organomodifiée.

Water-assisted extrusion of Polypropylene/Clay Nanocomposites: a comprehensive study

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Polymer

(accepted with modifications)

Work presented at the Belgian Polymer Group (BPG) Annual
Meeting, 2010 (Blankenberge, Belgium).

Abstract

Water-assisted extrusion process has been used to successfully prepare polypropylene (PP)/clay nanocomposites with high degree of clay delamination and markedly improved rheological, thermal and mechanical properties. PP-graft-maleic anhydride (PP-g-MA)-based nanocomposites and masterbatches were synthesized from untreated clay and organoclay, respectively, and fully characterized. The effects of using high-shear rates and water injection during the melt compounding were examined. A mechanism explaining the formation of such nanocomposites is then proposed. The best clay dispersion and properties improvements of PP-g-MA/organoclay nanocomposites and masterbatches were obtained using high-shear rates and water injection. PP-based nanocomposites were then synthesized by dilution of PP-g-MA-based masterbatches into neat PP. For comparison, nanocomposites were also prepared by a one-pot process where PP, PP-g-MA and organoclay are directly melt-blended with or without water injection. The nanocomposites prepared by dilution into PP of a masterbatch prepared through water-assisted extrusion showed the highest clay dispersion and consequently the best thermal, mechanical and rheological properties.

6.1 Introduction

In recent years, polymer/clay nanocomposites have become fashionable. The main reason of this interest is the enhancement of the polymer matrix properties that could be obtained with only a few percents of filler. In comparison to neat polymer matrix, polymer/clay nanocomposites usually exhibit higher mechanical and barrier properties and flame retardant behavior [1–5]. A few weight percents of layered silicate clays allow reaching similar properties than much higher amounts (20–40 %) of conventional filler (talc, glass fibers, calcium carbonate) [6–9].

Montmorillonite (MMT) is the most employed clay for the preparation of polymer/clay nanocomposites. MMT is a layered aluminosilicate mineral with sodium counterions present between the clay layers. MMT silicate layers present a high aspect ratio (length/thickness ratio) with their one nanometer thickness and hundreds nanometers length. They offer thus a large surface area for polymer/filler interactions. Naturally stacked into aggregates of several microns, MMT layers need to be separated and dispersed into the polymer matrix to obtain a nanocomposite.

The most usual way to produce polymer/clay nanocomposites is by melt-blending in an extruder because it is inexpensive, environmentally-friendly and straightforward [5, 10, 11]. Nanocomposites prepared by melt-blending are synthesized almost exclusively from organoclay to solve the lack of compatibility between the polymer and the clays [1, 2, 10, 12]. Organoclays are MMT in which the interlayer sodium counterions have been replaced by organic cationic surfactants, mostly alkylammoniums [12]. The introduction of surfactants increases the interlayer spacing and lowers the clay surface energy, thus facilitating the separation and dispersion of the clay layers into the polymer matrix.

Polypropylene (PP) is one of the most used matrix in polymer/clay nanocomposites due to its very large commercial importance [6]. PP/clay nanocomposites are usually prepared by melt-blending, using compatibilizers such as PP-graft-maleic anhydride (PP-g-MA) and organoclays [13–15]. Compatibilizers are required due to the huge polarity difference

between the polyolefin matrix and the clay. PP-g-MA allows wetting of the clay surface by hydrogen-bond interactions between the anhydride functions (acid functions when hydrolyzed) and the oxygen atoms at the surface of the silicate layers [16, 17].

Even when using organoclay and compatibilizers, PP/clay nanocomposites usually exhibit poor clay dispersion and, consequently, limited properties improvements are obtained. The main reason is the poor thermal stability of the alkylammonium-surfactants, which often decompose at extrusion temperatures leading to a collapse of the silicate layers [18–21].

Water-assisted extrusion was firstly described in a patent by DSM [22]. The DSM invention focuses on the preparation of polyamide (PA) nanocomposites by mixing in the melt phase a PA, a high aspect ratio particle (like a clay) and a liquid (preferably water). The mixing was carried out in a twin screw extruder equipped with a water injection system and a degassing zone. The recommended amount of injected water varies from 5 to 50 wt% and more preferably from 10 to 40 wt%. Exfoliated PA/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 -CONH- amide bond between repeating aliphatic units.

A research team from Toyota [23] reported a few years later the preparation of PA nanocomposites with an aqueous slurry of MMT which was melt-blended with PA using a laboratory extruder; the water release was removed by a vacuum pump. According to the authors, the slurry pumped into the extruder, is reduced in finer slurry drops. Water in droplets is evaporated on contact with molten PA and removed under vacuum, letting exfoliated clay layers fixed into PA. Thus exfoliated PA/MMT nanocomposites were successfully obtained, featuring mechanical properties close to those obtained for PA/organoclay nanocomposites. Nevertheless, the drawback of this clay slurry process, is the requirement of a huge amount of water (49 wt%) pumped into the

extruder to reduce the slurry viscosity.

The same Toyota's research team [24] improved the clay slurry process for the preparation of PP/organoclay nanocomposites from untreated MMT. Premixed PP, PP-g-MA, MMT and the quaternary ammonium salt were melt-blended into a twin screw extruder and water was then injected at a rate of 16.7 wt%. According to the authors, the clay organomodification occurs *in situ* by a cation exchange between sodium cations from MMT and the quaternary ammonium salts. Then PP-g-MA helps to disperse the stabilized clay into PP when water is evaporated. The resulting nanocomposite showed similar mechanical properties to a conventional PP/organoclay nanocomposite.

Based on the work of Toyota [23], Mai, Varlet and coworkers [25, 26] described the preparation of PA/untreated MMT nanocomposite by water-assisted melt-compounding in the presence of a much lower amount of water (18.4 wt% in place of 49 wt%). The resulting nanocomposite showed increased clay dispersion, mechanical properties and thermal stability in comparison with PA/MMT nanocomposite without water or PA/organoclay nanocomposite. This later was also extruded using water injection but neither the clay dispersion nor the mechanical properties could be improved. The authors attributed those results to the hydrophobic nature of the organoclay which cannot be wetted by water.

A few years later, Fedullo et al. [27, 28] developed in collaboration with DSM, a water-assisted melt-compounding process for PA/untreated MMT nanocomposites using a lab-scale high-shear twin-screw extruder. PA and MMT were introduced into the extruder and 0 to about 20 wt% water was injected. A better clay dispersion and a higher clay basal spacing were observed for the PA/MMT nanocomposite prepared with the aid of water. According to the authors, the water injected at high pressure and high temperature plays two roles. On the one hand, since water is miscible with PA in the extrusion conditions (high pressure and high temperature) [27–29], it modifies the fluidity and the polarity of

PA. On the other hand, water diffuses between MMT platelets and is adsorbed onto their surface, increasing the interlayer distance. These two effects allow PA to diffuse into MMT galleries and to be adsorbed onto MMT surface while water is desorbed through degassing.

Recently, Aloui et al. [30] investigated the elaboration of PP/untreated MMT nanocomposites by injecting PP-g-MA aqueous suspensions into molten PP. PP and MMT were melt blended under high-shear while commercial aqueous suspensions of PP-g-MA were introduced through the water injection system at 13 wt%. Different aqueous suspensions containing cationic or anionic surfactants and PP-g-MA were injected during extrusion to promote clay dispersion. Even if full exfoliation is not obtained for these nanocomposites using injection of aqueous suspensions, clay intercalation evidences are observed by X-ray diffraction and the thermal, rheological and mechanical properties of the materials remain comparable to a conventional PP/organoclay nanocomposite.

Lastly, Mainil et al. [31] reported a water-assisted extrusion process for poly(styrene-co-acrylonitrile) (SAN, containing 25 wt% of AN) nanocomposites with untreated MMT (Cloisite Na, labeled CNa) and organoclay in which the onium ion possesses an alkyl chain, a methyl group and two hydroxyethyl groups (Cloisite 30B, labeled C30B). Water was introduced at a rate of 23 wt%. The goal of the research was to investigate the ability of the water-assisted extrusion process to promote the clay dispersion with a less polar polymer than PA. For CNa, the clay dispersion was largely improved using the water assisted extrusion process but the lack of chemical compatibility between untreated MMT and SAN hindered the improvement of thermal and mechanical properties. For C30B, the use of the water assisted extrusion process markedly improved the clay dispersion. The thermal and mechanical characterizations evidenced the superiority of the SAN/C30B nanocomposites extruded with water.

The present paper discusses the preparation of PP/clay nanocomposites by the previously described water-assisted extrusion process and the

study of their structural, thermal, rheological and mechanical properties. PP-g-MA/clay nanocomposites and masterbatches from untreated clay (CNa) and organoclay (C30B) with or without water injection and at low- or high-shear rates, have been synthesized and characterized. The first part of this work is a comprehensive study on the possible interactions occurring between the untreated MMT or the organoclay and the PP-g-MA with and without the help of water.

In the second part of this work, PP/clay nanocomposites are produced by dilution of PP-g-MA/clay masterbatches into PP, and compared with nanocomposites prepared by water-assisted direct melt-compounding of PP, PP-g-MA and clay (called the one-pot process).

The influence of shear rate and water-assisted extrusion process is studied at different stages of the PP/clay nanocomposites preparation and a mechanism explaining the formation of PP/MMT nanocomposites through water-assisted extrusion is proposed.

6.2 Experimental

6.2.1 Materials

PP Moplen HF500N was purchased from Basell and PP-g-MA Polybond 3200 (labeled Plb) from Chemtura. Untreated sodium-Montmorillonite (Cloisite Na, labeled CNa) and sodium-Montmorillonite modified with bis(2-bis hydroxyethyl) methyl tallow ammonium chloride (Cloisite 30B, labeled C30B) were purchased from Southern Clay Product.

6.2.2 Sample preparation

All references and composites were prepared in a co-rotating twin-screw extruder Krupp WP ZSK25. The extruder screw length is 1000 mm with a L/D ratio of 40. The barrel temperature (T) is fixed at 180 °C for PP-g-MA-based samples and 200 °C for PP-based ones. Water, when used, was pumped into the extruder in the high compression zone¹. The

¹A scheme of the extruder is given in Appendix to Chapter 6

special design of the screw allows the pressure to increase up to 125 bars in this zone which maintains the water liquid [28]. The water is degassed in the transport zone and fully removed using a vacuum pump. The throughput (TP), the screw speed (SP) and the water injection rate (W) were adapted to the experience. PP-g-MA-based references, nanocomposites and masterbatches were processed at a screw speed of 200 or 1000 RPM and a throughput of 7 or 21 kg/h. The water injection rate was adapted to the screw speed to ensure a constant amount of water (5.7 wt%) for the different experiments. PP-based references and nanocomposites were extruded at a screw speed of 200 RPM and a throughput of 7 kg/h. The extruded samples were immediately quenched into cold water and pelletized.

PP-g-MA-based references, nanocomposites and masterbatches (Table 6.1) contain 0, 5 and 15 wt% of clay (CNa or C30B) in inorganic content, respectively. PP-based references and nanocomposites contain 0 and 3 wt% of C30B clay in inorganic content, respectively (Table 6.2). PP-g-MA-based references are labeled R, nanocomposites NC-A (from CNa) or NC-B (from C30B) and masterbatches MB-B (from C30B). PP-based references are labeled PP-Plb. Nanocomposites made by dilution of PP-g-MA-based masterbatches into PP are labeled NC-MB-B and nanocomposites made by the one pot process are labeled NC-OP-B.

After extrusion, all samples were injection-molded using a Krauss-Maffei type KM 80-160E injection molding machine into standard dog-bone specimens (ASTM 527). The barrel temperatures ranged within 170-200 °C and the mold temperature was kept at 25 °C. Before injection-molding, pelletized samples were dried for 24h at 70 °C under vacuum.

6.2.3 Characterizations

All characterizations were performed onto injection-molded dog-bone specimens. Raw Plb and PP were also injection-molded into dog-bone specimens for analysis.

Table 6.1: Composition of the PP-g-MA-based references, nanocomposites and masterbatches samples. Legend: Inorganic Content (IC), Screw Speed (SS), Throughput (TP), Water injection rate (W).

Samples	Clay	Clay (wt%)	IC (wt%)	SS (RPM)	TP (kg/h)	W (ml/min)
R1	/	0	0	200	7	0
R2	/	0	0	200	7	7
R3	/	0	0	1000	21	0
R4	/	0	0	1000	21	21
NC-A1	CNa	5.5	5	200	7	0
NC-A2	CNa	5.5	5	200	7	7
NC-A3	CNa	5.5	5	1000	7	0
NC-A4	CNa	5.5	5	1000	7	21
NC-B1	C30B	7.1	5	200	7	0
NC-B2	C30B	7.1	5	200	7	7
NC-B3	C30B	7.1	5	1000	21	0
NC-B4	C30B	7.1	5	1000	21	21
MB-B1	C30B	21	15	200	7	0
MB-B2	C30B	21	15	200	7	7
MB-B3	C30B	21	15	1000	21	0
MB-B4	C30B	21	15	1000	21	21

Table 6.2: Composition of the PP-based references and nanocomposites samples. Legend: Masterbatch (MB), Inorganic Content (IC), Water injection rate (W).

Samples	PP (wt%)	Plb (wt%)	C30B (wt%)	MB (wt%)	IC (wt%)	W (ml/min)
PP-Plb1	85	15	0	0	0	0
PP-Plb2	85	15	0	0	0	7
NC-OP-B1	81	15	4	0	3	0
NC-OP-B2	81	15	4	0	3	7
NC-MB-B3	80	0	0	20	3	0
NC-MB-B4	80	0	0	20	3	0

Structural characterizations

X-ray diffraction (XRD). The interlayer spacing of the nanocomposites was measured by XRD on a Bruker D8 Advance diffractometer using $\text{CuK}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) at 40 kV and 30 mA.

Transmission electron microscopy (TEM). Clay dispersion of nanocomposite samples was examined on TEM pictures. Samples were ultra-microtomed at ambient temperature with a Reichert Microtome and collected on a 300 mesh copper grid. TEM pictures were recorded with a LEO 922 microscope operating at 200 kV.

Fourier Transform Infrared (FTIR) spectroscopy. FTIR spectra were recorded on a Nicolet Nexus 870 FTIR spectrometer on compression-molded films in transmission mode by collecting 16 scans at a resolution of 4 cm^{-1} over a spectral range from 4000 to 400 cm^{-1} . Films were obtained by compression-molding of one head of the injection-molded dog-bone specimens. The spectra were normalized by setting the peak height of the 2723 cm^{-1} absorption band (characteristic C-H stretching of PP) to an absorbance of 1.

Rheological, Thermal and Mechanical characterizations

Rheology. Rheological measurements were carried out in an oscillatory mode on a Bohlin Gemini II rheometer equipped with a parallel plate geometry using 25 mm diameter plates. Frequency sweep tests were performed on compression-molded samples of about 1.0 mm in thickness at a strain rate of 10 % for references and nanocomposites and 5 % for masterbatches. Testing temperature was 180 °C for PP-g-MA/clay nanocomposites and 200 °C for PP/clay nanocomposites. Experimental conditions were preliminary adjusted to work in the linear viscoelastic range.

Thermogravimetric analysis (TGA). The thermal stability of the references and composites was studied by TGA. The analyses were performed on a Mettler Toledo TGA/SDTA 851e using a heating rate of 20 °C/min under air or nitrogen atmosphere (100 ml/min) from 25

to 1000 °C. TGA results are presented as temperatures at 5 % (T-5), 10 % (T-10) and 50 % (T-50) weight loss under air atmosphere and each value is the average of three experiments. T-5, T-10 and T-50 are usually considered as the initial decomposition temperature, the onset and the midpoint of the degradation, respectively [32].

Mechanical testing. Tensile tests were performed on a Zwick tensile machine using a 50 kN force sensor and an extensometer for strain measurement. Tests were conducted at a crosshead speed of 5 mm/min for Young's modulus measurement and at 50 mm/min for elongation measurement.

6.3 Results and discussion

6.3.1 PP-g-MA-based references, nanocomposites and masterbatches

Understanding the possible interactions occurring between PP-g-MA and the CNa untreated MMT or the C30B organoclay with and without the help of higher shear rates and/or water injection has been first investigated. The morphology of these PP-g-MA-based references and nanocomposites is examined by XRD and TEM and the interactions between the clay and PP-g-MA are investigated by FTIR. The PP-g-MA-based references and nanocomposites are also characterized using TGA, rheology and mechanical testing, in order to understand the observed structural changes onto the references and nanocomposites properties.

Structural characterizations

The nanocomposites are characterized by XRD to follow the evolution of the clay basal spacing. Figures 6.1a and 6.1b show the X-ray diffraction patterns of the PP-g-MA-based nanocomposites from CNa and C30B, respectively. The starting CNa exhibits only a (001) basal spacing centered at 1.24 nm ($7.1^\circ 2\theta$). The basal spacing measured for

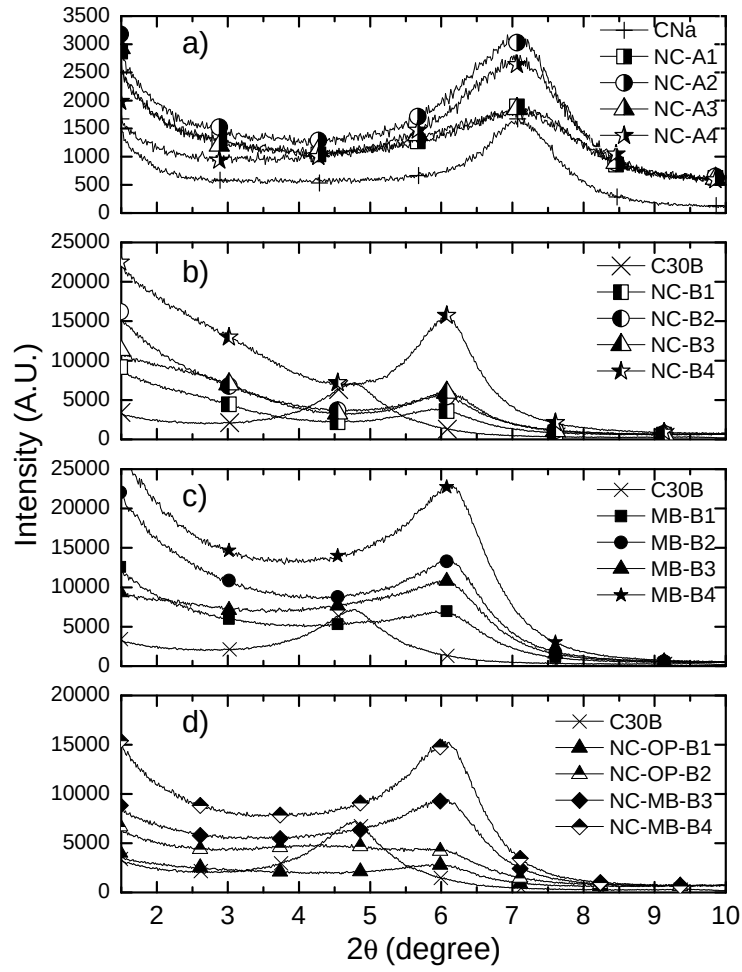


Figure 6.1: XRD patterns of PP-g-MA-based nanocomposites from CNa (a) and C30B (b), of PP-g-MA/C30B masterbatches (c) and of PP/C30B nanocomposites (d).

CNa corresponds to the presence of one layer of water in the clay interlayer [33, 34]. All PP-g-MA/CNa microcomposites (NC-A1 to NC-A4) present the same clay basal spacing as CNa, indicating that no intercalation of CNa by Plb occurs whatever the extrusion conditions. The starting C30B exhibits only a (001) basal spacing centered at 1.88 nm ($4.7^\circ 2\theta$). In PP-g-MA/C30B nanocomposites (NC-B1 to NC-B4), the basal spacing of the C30B disappears, a new reflexion appears at 1.42 nm ($6.2^\circ 2\theta$) and a shoulder can be seen around 3–3.5 nm ($2.5\text{--}3^\circ 2\theta$). Moreover, for NC-B2 and NC-B4, a gradual increase in the diffraction intensity toward low angles is observed. The new peak at 1.42 nm indicates that part of the C30B silicate layers has collapsed. The collapse results from surfactant degradation in C30B and has already been observed by other authors [35, 36]. The shoulder around 3–3.5 nm means that another part of the C30B silicate layers has been intercalated. The increase in the diffraction intensity toward low angles is commonly attributed to completely dispersed clay layers [13, 37]. It indicates that NC-B2 and NC-B4 exhibit a mixed distribution of completely dispersed clay layers with intercalated and collapsed clay stacks while NC-B1 and NC-B3 exhibit only intercalated and collapsed clay stacks.

TEM analyses are performed to examine the clay layers dispersion in the nanocomposites. TEM pictures of PP-g-MA/CNa samples (not shown) only present large clay aggregates of several microns. Accordingly, PP-g-MA/CNa samples are called microcomposites instead of nanocomposites. For these microcomposites, neither the high-shear extrusion nor the water injection can help to increase the clay dispersion into the polymer matrix.

Figure 6.2 presents TEM pictures of PP-g-MA/C30B nanocomposites. NC-B1 (Figure 6.2a) shows a highly heterogeneous morphology, composed of huge clay stacks and few individual clay platelets. NC-B3 (Figure 6.2c) shows better clay dispersion than NC-B1. The use of high-shear rates mainly breaks the large clay aggregates and generates homogeneously distributed small clay stacks. NC-B2 (Figure 6.2b) still

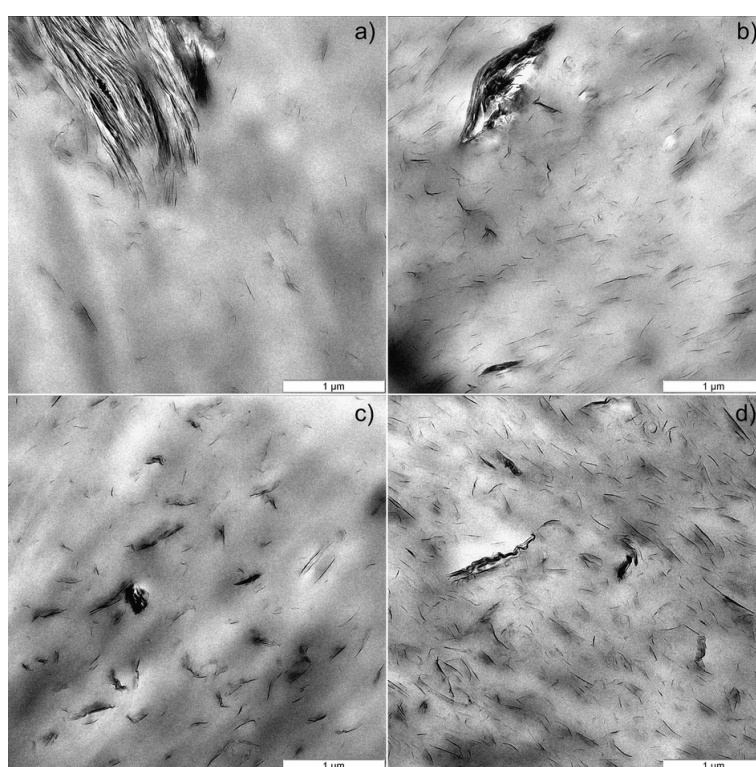


Figure 6.2: PP-g-MA-based TEM pictures of a) NC-B1, b) NC-B2, c) NC-B3 and d) NC-B4 at a magnification of 5,000.

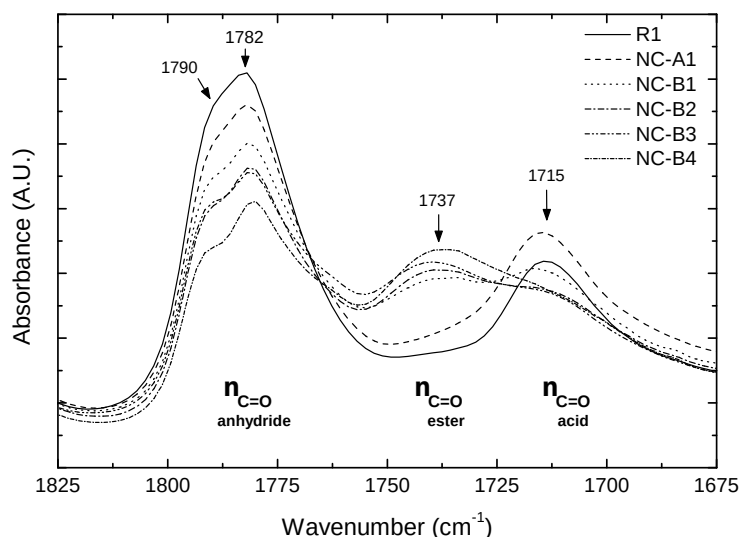


Figure 6.3: FTIR spectra of R1, NC-A1, and NC-B1 to NC-B4 samples.

exhibits micron-sized clay stacks, but homogeneously-distributed individualized clay layers are mainly observed. The use of water injection markedly improves the C30B dispersion. The best clay dispersion is observed when combining high-shear rates with water injection in NC-B4 (Figure 6.2d) where the clay platelets are almost all individualized with few small clay stacks. Contrary to PP-g-MA/CNa microcomposites, in the case of PP-g-MA/C30B nanocomposites high-shear rates and, in a larger extent, water injection clearly favor the dispersion of C30B organoclay into the PP-g-MA matrix. XRD measurements and TEM pictures are in good agreement since only NC-B2 and NC-B4 exhibit completely dispersed clay layers.

Mechanistic considerations

The interaction between the clay and the PP-g-MA matrix has been further investigated by FTIR. Figure 6.3 shows infrared spectra enlarge-

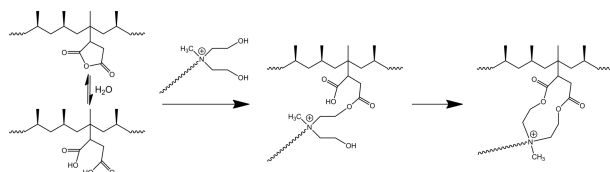


Figure 6.4: Esterification reaction between $-COOH$ of PP-g-MA and $-OH$ of C30B's surfactant.

ment of the respective carbonyl regions for R1, NC-A1, and NC-B1 to NC-B4 samples. R2 to R4 and NC-A2 to NC-A4 spectra are not shown since they are similar to R1 and NC-A1, respectively. Two main absorption bands can be observed in the $1675\text{--}1825\text{ cm}^{-1}$ carbonyl region for R1 and NC-A1: the maleic anhydride band (carbonyl symmetric stretching) around $1780\text{--}1790\text{ cm}^{-1}$ and the carboxylic acid band (carbonyl stretching) around 1715 cm^{-1} . The presence of a carboxylic acid band is explained by the hydrophilicity of the PP-g-MA anhydride moieties, which absorb ambient moisture and form carboxylic diacid functions [38]. No band shift is observed for NC-A1 in comparison with the R1 spectrum. For all PP-g-MA/C30B nanocomposites, a new band appears around $1735\text{--}1740\text{ cm}^{-1}$ assigned to an ester function (carbonyl stretching). The appearance of an ester band and the related intensity decrease of the anhydride band result from a Fischer esterification reaction occurring between hydroxyl functions of C30B and carboxylic acid functions of PP-g-MA (Figure 6.4). As a matter of fact, for all PP-g-MA/C30B nanocomposites, there is also a reduction of the acid band intensity. The two carboxylic acid functions of PP-g-MA may react with the two hydroxyl functions of C30B, the second esterification being an entropically favored intramolecular reaction. Indeed, if only one esterification reaction occurs, an increase of the acid band should be observed. Ranking NC-B samples on their ester band intensity and anhydride and acid bands decrease gives $NC-B1 < NC-B2 \approx NC-B3 < NC-B4$. In PP-g-MA/C30B nanocomposites, the best clay dispersion is

observed for NC-B4 which displays the most intense ester band.

On that experimental basis, a hypothesis on the role of the water injection can be developed. Water injected into the extruder where PP-g-MA and C30B are melt-blended, remains liquid and creates an aqueous suspension of C30B which is strongly melt-mixed with PP-g-MA. Moreover, considering that the C30B surfactant contains hydroxyl groups and that high temperature and high pressure occur inside the extruder, a partial delamination of the C30B clay layers can be obtained. Thus after water degassing, a more homogeneous distribution of the C30B platelets into molten PP-g-MA can be reached. Furthermore, injected water hydrolyzes anhydride functions of PP-g-MA into carboxylic diacid functions. Since the Fisher esterification is acid-catalyzed, more esterification reactions can take place between PP-g-MA and C30B surfactant. The role of water is then double: it directly increases C30B layers distribution during the melt-blending and it indirectly favors bonding between PP-g-MA and C30B through acid-catalyzed esterification.

Rheological, Thermal and Mechanical Characterizations

Rheological characterization is used to evaluate the dispersion state of the filler. Indeed, the melt flow behavior is quite sensitive to the structure, particle size and shape and surface properties of a dispersed phase [39, 40]. When adding fillers to a polymer matrix, that create favorable filler-matrix interactions, an increase of the elastic modulus (G') and of the complex viscosity (η^*) at low frequencies is observed. If a percolating mesoscopic filler network is formed, an elastic modulus plateau most often appears and the complex viscosity continuously raises at low frequencies.

Figures 6.5a, 6.5b and 6.5c show the elastic modulus and complex viscosity curves of PP-g-MA-based references, PP-g-MA/CNa microcomposites and PP-g-MA/C30B nanocomposites, respectively. There is no significant difference in G' or η^* curves for PP-g-MA-based references which all show typical liquid-like behavior (at low frequencies, G' has

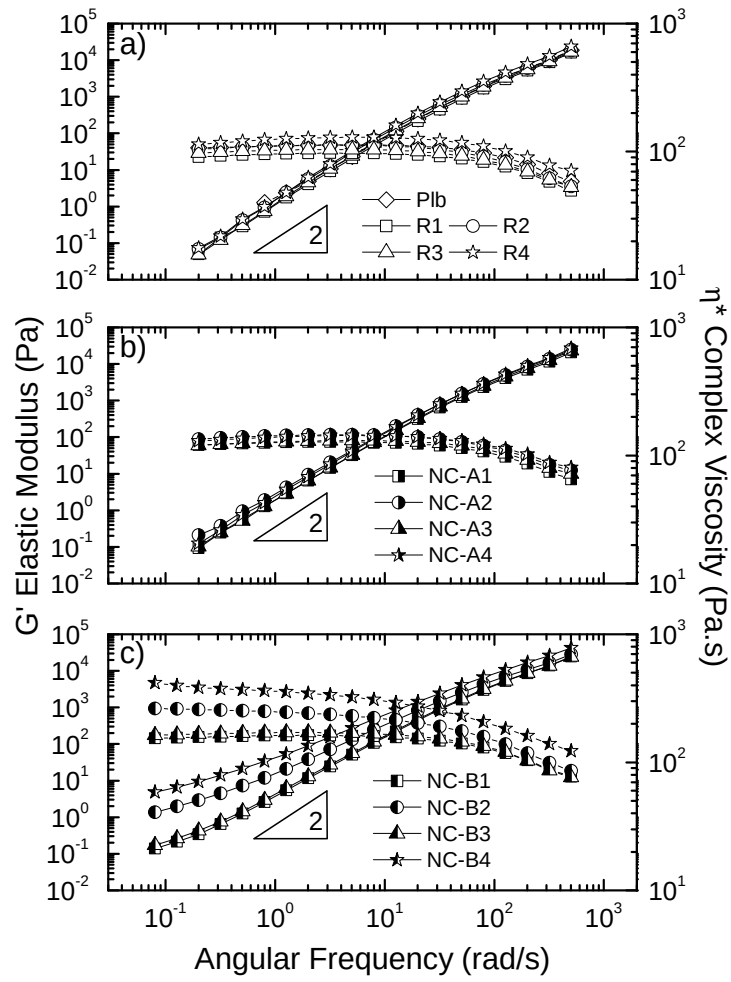


Figure 6.5: Elastic modulus and complex viscosity at 180 °C as a function of the frequency of PP-g-MA-based references and nanocomposites.

a slope close to 2 and η^* reaches a Newtonian plateau). The G' or η^* curves of PP-g-MA/CNa microcomposites are slightly increased compared to PP-g-MA references. However, as PP-g-MA references, they all exhibit a typical liquid-like behavior. No significant difference is observed between them (their G' slopes at low frequencies are around 1.8–1.9). This slight increase of rheological properties of PP-g-MA/CNa microcomposites is in agreement with the poor dispersion of CNa which consequently brings weak matrix reinforcement. On the contrary, PP-g-MA/C30B nanocomposites show higher G' and η^* curves than PP-g-MA references (and PP-g-MA/CNa microcomposites). Moreover their G' curves show a decrease of the frequency dependence at low frequencies. This is the consequence of the better clay dispersion obtained using C30B, instead of CNa, which consequently induces higher matrix reinforcement. Even if NC-B3 exhibits a better clay dispersion than NC-B1 according to the TEM characterization, the rheological behavior of both samples is similar.

Rheological characterizations thus confirm the previous structural observations showing that high-shear rates mainly break clay stacks into more homogeneously-distributed smaller ones without increasing the extent of completely dispersed clay layers. Therefore, almost no difference is observed in their rheological behavior. NC-B2 and NC-B4, show higher G' and η^* curves than their respective PP-g-MA/C30B nanocomposites prepared without water. The G' slopes at low frequencies are 0.86 for NC-B2 and 0.78 for NC-B4. Thus, the use of water injection when producing PP-g-MA/C30B nanocomposites markedly lead to the rheological properties improvement, in agreement with their good clay layers dispersion. The combination of high-shear rates and water injection highly enhances the rheological properties of PP-g-MA/C30B nanocomposites.

Higher thermal stability is commonly observed when clay platelets are well-dispersed into the polymer matrix, as a result of hindered out-diffusion of the volatile decomposition products and also of char for-

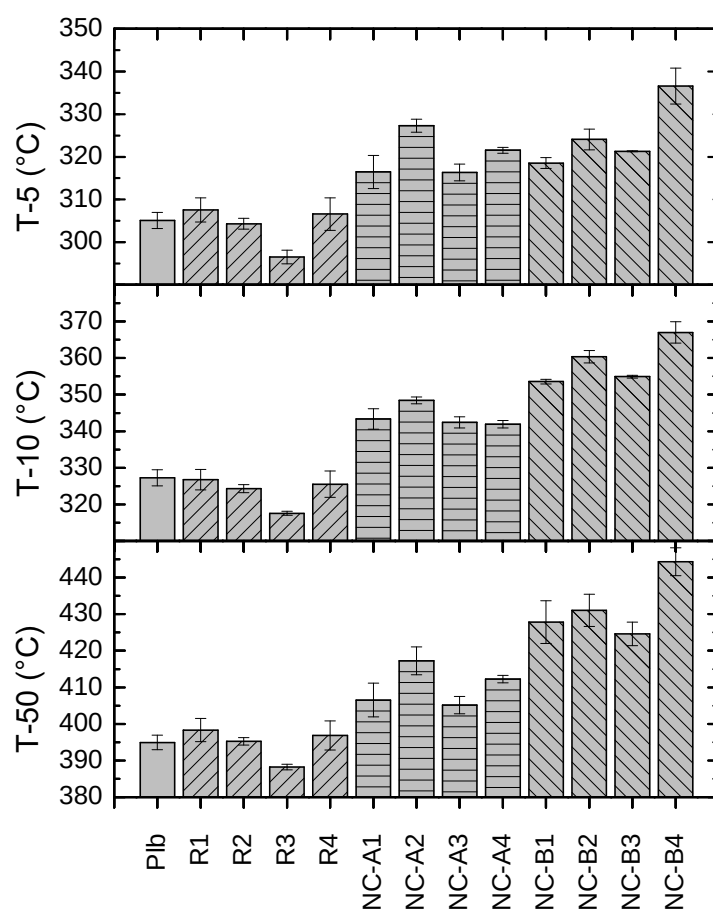


Figure 6.6: Temperatures at 5% (T-5), 10% (T-10) and 50% (T-50) weight loss under air atmosphere for PP-g-MA-based references and nanocomposites.

mation that acts as a physical barrier between the polymer and the oxidative medium [1]. Figure 6.6 presents the TGA results for PP-g-MA-based references and nanocomposites. Except for R3, the thermal stability of PP-g-MA-based references is not significantly different from as-received Plb. The lower thermal stability of R3 can be explained by the high-shear rates applied, which raise the melt temperature and could consequently increase the thermo-mechanical degradation. Compared to Plb, PP-g-MA/CNa samples exhibit a slight but significant increase of their thermal stability despite the poor CNa dispersion into Plb. These thermal stability improvements are comparable with those observed by Villaluenga et al. for PP filled with CNa [41]. In opposition to the water injection, higher shear rates do not increase the thermal stability of PP-g-MA/CNa microcomposites.

PP-g-MA/C30B samples show superior thermal stability than PP-g-MA/CNa samples. This is consistent with the better clay dispersion obtained in PP-g-MA/C30B nanocomposites than in PP-g-MA/CNa microcomposites. As for PP-g-MA/CNa, in the absence of water, high-shear rates do not change the thermal stability of PP-g-MA/C30B nanocomposites. The higher clay dispersion reached in PP-g-MA/C30B nanocomposites using water injection, hinders more efficiently the out-diffusion of the volatile decomposition products. NC-B4 exhibits thus the greatest thermal stability. Contrary to PP-g-MA/CNa microcomposites, a synergistic effect by using high-shear rates and water injection for PP-g-MA/C30B nanocomposites is marked. This result is in good agreement with the rheological measurements.

Mechanical reinforcement is expected when clay platelets are well-dispersed into the polymer matrix. Especially, Young's modulus commonly increases and depends on the filler dispersion and the interfacial interactions. Indeed, enlarging the interface between the matrix and the filler increases the volume of polymer chains influenced by the rigid clay platelets.

Figure 6.7 shows the relative Young's modulus (E') from tensile tests

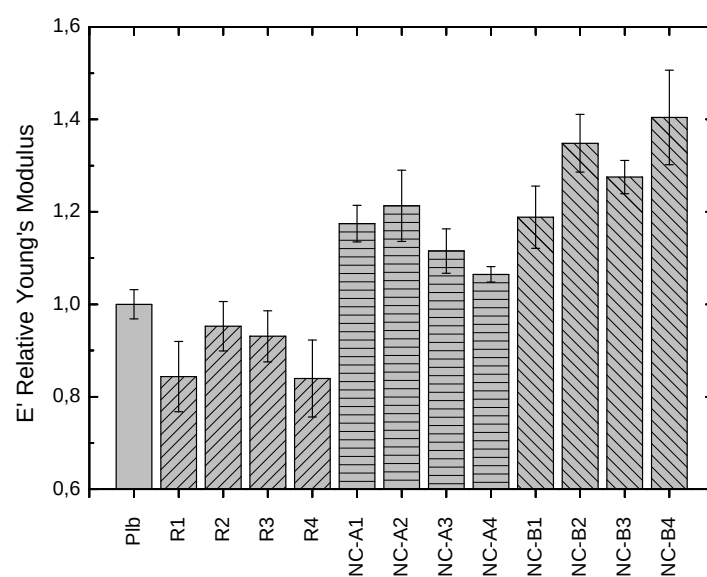


Figure 6.7: Relative Young's modulus of PP-g-MA-based references and nanocomposites.

of PP-g-MA-based references and nanocomposites. All PP-g-MA-based references have lower E' values than as-received Plb and all PP-g-MA/CNa microcomposites exhibit higher E' than starting PP-g-MA. Despite their poor clay dispersion, their E' is increased from 6 to 21% in comparison with starting Plb. Rheological, thermal and mechanical properties, all agree that NC-A2 shows the better properties improvement in PP-g-MA/CNa microcomposites. These modulus improvements are comparable with those obtained for thermoplastic polyolefins filled with talc [8]. This is in good agreement with TEM pictures of PP-g-MA/CNa microcomposites (not shown) where only large micron-sized clay aggregates are observed.

In absence of water and with low shear rates, the same mechanical reinforcement is basically obtained with CNa (NC-A1) or C30B (NC-B1). Indeed, except that NC-B1 exhibits a few completely dispersed clay layers, the clay dispersion in NC-A1 and NC-B1 is mainly composed of very large clay stacks. In opposition to the rheological results, the Young's modulus of NC-B3 is significantly higher than the one of NC-B1. High-shear rates thus increase the mechanical reinforcement of the matrix in PP-g-MA/C30B nanocomposites. This can be explained by the presence of smaller clay stacks which offer more clay surface available for interaction with the PP-g-MA matrix. The use of water injection for producing PP-g-MA/C30B nanocomposites again leads to further mechanical reinforcement since NC-B2 and NC-B4 show higher E' values than NC-B1 and NC-B3, respectively. As for the rheological properties, a synergistic effect by using high-shear rates and water injection is observed on the mechanical properties of PP-g-MA/C30B nanocomposites.

PP-g-MA-based Masterbatches

Since PP-g-MA/CNa microcomposites exhibit poor clay dispersion and weak properties improvement, masterbatches are only considered by using C30B. Four PP-g-MA/C30B masterbatches have been extruded similarly to the four PP-g-MA/C30B nanocomposites (Table 6.1) and

characterized by XRD and rheology.

Figure 6.1c shows the X-ray diffraction patterns of the PP-g-MA/C30B masterbatches. All samples show only one reflexion at 1.42 nm ($6.2^\circ 2\theta$) indicating that C30B silicate layers have collapsed due to the surfactant decomposition. A gradual increase in the diffraction intensity toward low angles is observed for MB-B1, MB-B2 and MB-B4 indicating a mixed distribution of collapsed clay stacks and completely dispersed clay layers.

Figure 6.8 shows G' and η^* curves of PP-g-MA/C30B masterbatches. Despite the high clay amount, MB-B1 still exhibits a Newtonian plateau (on its η^* curve) and a G' slope of 0.93 at low frequencies. Using high-shear rates increase G' and η^* curves of MB-B3. However, this increase is higher with water injection (MB-B2). Even if both MB-B2 and MB-B3 have a G' slope of 0.76 in the terminal zone, the effect of water injection appears more important than high-shear rates. A further raise of G' and η^* curves is obtained when combining water injection and high-shear rates. MB-B4 presents an important reduction of the frequency dependence on its G' curve with a G' slope of 0.58, while its η^* curve continuously increases at low frequencies, indicating that the percolation threshold is reached. As for PP-g-MA/C30B nanocomposites, the best improvement is obtained when combining high-shear rates and water injection.

Based on the properties improvement of PP-g-MA/C30B nanocomposites and masterbatches, the MB-B4 sample has been selected for dilution into PP matrix in the next step of the work. The further results will be compared to MB-B3 considered as a reference to evaluate the influence of water.

6.3.2 PP-based references and nanocomposites

This second part of the work is focused on the production and characterization of PP-based nanocomposites by dilution of PP-g-MA-based masterbatches into neat PP. The selected masterbatch, MB-B4, is di-

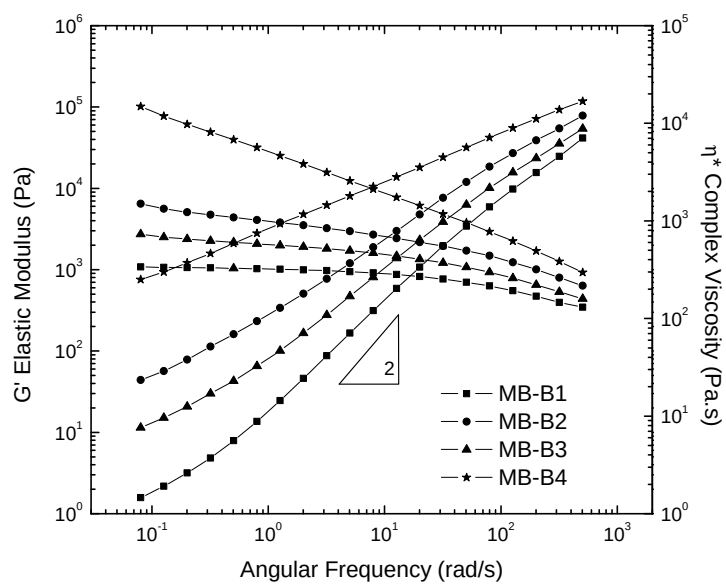


Figure 6.8: Elastic modulus and complex viscosity at 180 °C as a function of the frequency for PP-g-MA-based masterbatches.

luted into PP and the resulting PP-based nanocomposite is labeled NC-MB-B4. Similarly, MB-B3 diluted into PP is named NC-MB-B3 and used as the control without water. The relevance of the masterbatch dilution process will be confronted to the one-pot process in which PP, PP-g-MA and clay are directly melt-compounded together in one step to furnish the PP-based nanocomposite labeled NC-OP-B1. Moreover, another sample is considered, made by direct melt-compound of PP, PP-g-MA and clay with water injection (NC-OP-B2) to study the effect of water injection when the main matrix is PP.

Structural characterizations

Figure 6.1d shows the XRD patterns of PP/C30B nanocomposites. NC-MB-B3 and NC-MB-B4 patterns are similar to the one of MB-B3 and MB-B4 but only MB-B4 shows a gradual increase in the diffraction intensity toward low angles, which is attributed to completely dispersed clay layers. After dilution of the masterbatch, the reflexion still present at 1.42 nm ($6.2^\circ 2\theta$) in those nanocomposites suggests that the collapsing of C30B clay layers is non-reversible. In NC-OP-B1, the basal spacing of C30B disappears and the reflexion at 1.42 nm ($6.2^\circ 2\theta$) indicates a collapsing of C30B silicate layers due to the surfactant decomposition. No increase of basal spacing is detected. When using water injection in NC-OP-B2, two reflexions appear at 1.42 nm ($6.2^\circ 2\theta$) and around 2.13 nm ($4.15^\circ 2\theta$) indicating that C30B silicate layers are partially intercalated.

TEM pictures of PP/C30B nanocomposites are shown in Figure 6.9. NC-OP-B1 exhibits only large micron-sized clay aggregates. When using water injection in the one-pot process for NC-OP-B2, a few dispersed clay layers with small stacks are observed but still accompanied with micron-sized clay aggregates. The clay dispersion in NC-OP-B2 is slightly better than in NC-OP-B1 and comparable to the one of NC-MB-B3. The best clay dispersion in PP-based nanocomposites is obtained for NC-MB-B4 where well-distributed, completely dispersed clay layers and small stacks are exclusively observed. Based on TEM pictures ex-

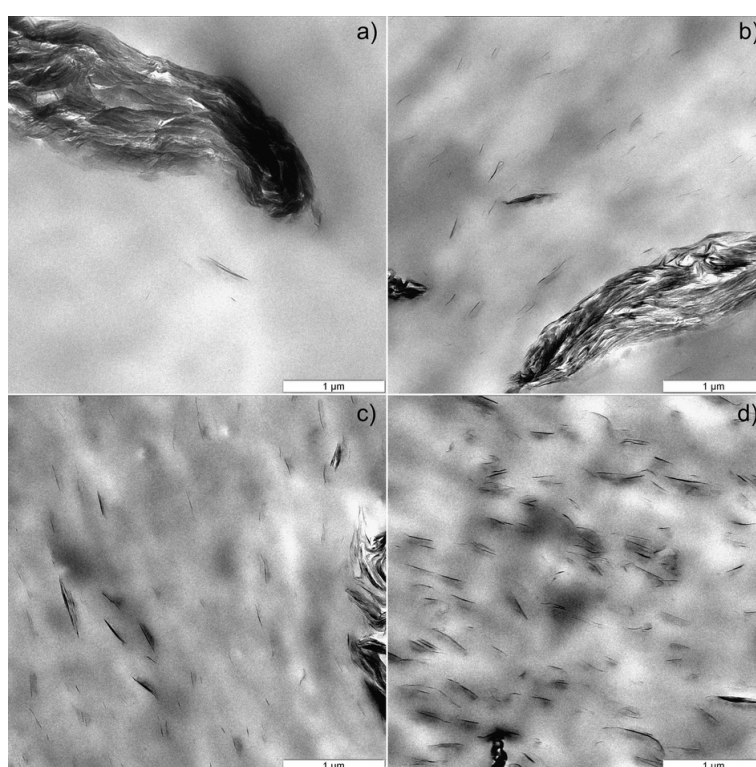


Figure 6.9: PP-based TEM pictures of a) NC-OP-B1, b) NC-OP-B2, c) NC-MB-B3 and d) NC-MB-B4 at a magnification of 5,000.

amination of PP/C30B nanocomposites, the masterbatch process leads to a better clay dispersion than the one-pot process.

Considering both on XRD and TEM results, it can be noticed that the effect of the water injection on the clay dispersion is much less important in PP/C30B nanocomposites prepared by the one-pot process than in PP-g-MA/C30B nanocomposites. The raise of completely dispersed clay layers is markedly more important in NC-B2 than in NC-OP-B2 comparatively to with their respective NC-B1 and NC-OP-B1 reference without water injection. The polarity of the main matrix seems to be crucial when using a water-assisted extrusion process. This can explain the larger extent of individual clay layers obtained for NC-MB-B4 prepared by the masterbatch dilution process regarding NC-OP-B2 prepared by the one-pot process.

Rheological, Thermal and Mechanical Characterizations

Elastic modulus and complex viscosity curves of PP-based references and nanocomposites are presented in Figure 6.10. Only NC-MB-B4 shows a significant increase of the G' and η^* curves in comparison with the other samples. Moreover the G' curve displays a decrease of the frequency dependence at low frequencies with a slope of 1.19. NC-OP-B1, NC-OP-B2 and NC-MB-B3 exhibit all similar G' and η^* curves to starting PP, but nevertheless higher than PP/PP-g-MA references (PP-Plb1 and PP-Plb2). These results are in excellent agreement with the clay dispersions observed on TEM pictures. The best rheological properties are observed for NC-MB-B4, the PP/C30B nanocomposite prepared from dilution of the water-assisted masterbatch, which features the best clay dispersion. The G' and η^* curves of PP-Plb1 and PP-Plb2, due to the presence of Plb, are reduced in comparison with as-received PP and their G' slope at low frequencies is around 1.75, a value slightly higher than the 1.56 slope recorded for PP. PP-Plb2 curves are less reduced than the PP-Plb1 ones due to the lubricant effect of water, which reduces the thermo-mechanical chain degradations. This lubricant

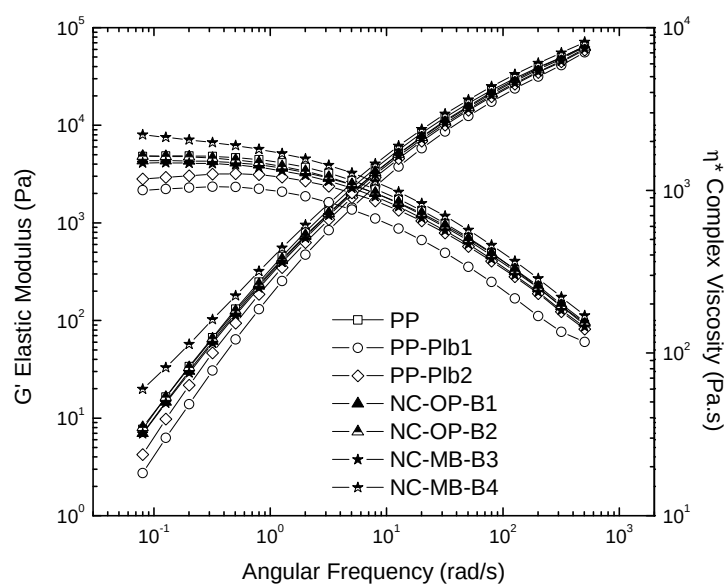


Figure 6.10: Elastic modulus and complex viscosity at 200 °C as a function of the frequency for PP-based references and nanocomposites.

effect is also encountered when extruding PP alone with water injection (results not shown).

Figure 6.11 presents the TGA results for PP-based references and nanocomposites. The thermal behavior of both PP-Plb references is quite similar to as-received PP indicating that Plb does not affect the thermal stability of PP. NC-OP-B1, NC-OP-B2 and NC-MB-B3 behave similarly and show higher thermal stability than PP. NC-MB-B4 shows the best thermal stability indicating an increase of the hindered out-diffusion of the volatile decomposition products due to a better clay dispersion. These results are in good agreement with the morphological observations and the rheological measurements.

Figure 6.12 shows the relative Young's modulus (E') and the elongation from tensile tests of PP-based references and nanocomposites. No difference in E' value is observed in the absence of clay for PP-based references and as-received PP. However both PP-Plb1 and PP-Plb2 break at an elongation superior to 600 %, a property explained by the plastification effect of PP-g-MA which has a lower molar mass than PP. NC-OP-B1, NC-OP-B2 and NC-MB-B3 show a similar increase of E' of about 30–35 %, while NC-MB-B4 shows an increase of E' of approximately 65–70 %. These Young's modulus values of PP/C30B nanocomposites are consistent with the morphological, rheological and thermal results. All PP/C30B nanocomposites break at lower elongation rates (around 30–50 %) than the corresponding references. The mineral fillers such as layered silicates, are indeed well known to decrease the ductility of the polymers [5].

6.4 Conclusions

PP-based nanocomposites with a high level of clay delamination and very significant properties improvement have been successfully prepared through dilution into neat PP of PP-g-MA-based masterbatches synthesized by a water-assisted extrusion process. Water injection and high-

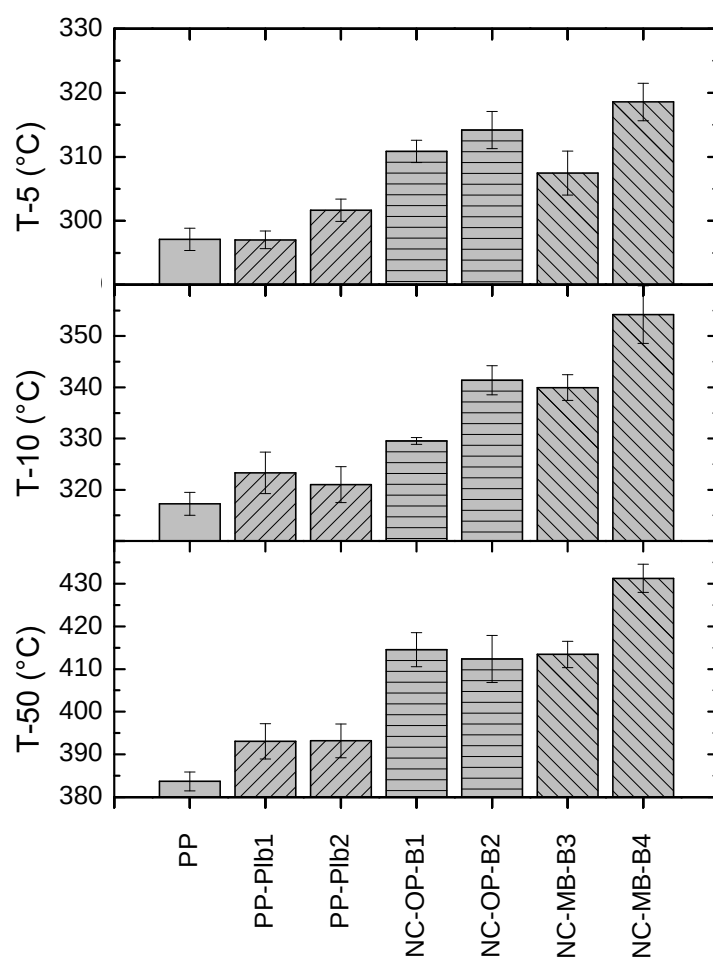


Figure 6.11: Temperatures at 5% (T-5), 10% (T-10) and 50% (T-50) weight loss under air atmosphere for PP-based references and nano-composites.

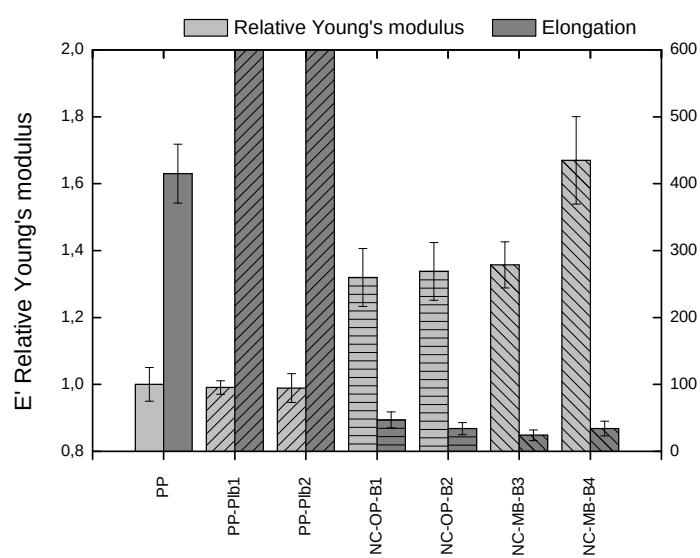


Figure 6.12: Relative Young's modulus and elongation for PP-based references and nanocomposites.

shear rates have a modest impact on the properties of PP-g-MA-based references and nanocomposites of untreated clay. However, for PP-g-MA-based nanocomposites and masterbatches synthesized with Cloisite 30B organoclay, better clay dispersion and important properties improvement have been obtained using high-shear rates and furthermore using water injection. Moreover, the combined use of water injection and high-shear rates showed a remarkable synergistic effect. In PP-g-MA/Cloisite 30B nanocomposites, an esterification reaction occurred between the hydroxyl function of Cloisite 30B organoclay surfactant and the carboxylic acid of PP-g-MA resulting from the anhydride hydrolysis. We have identified two main roles played by water on the clay dispersion of these nanocomposites. Firstly, water directly increases the clay dispersion during the melt-blending step by creating an aqueous suspension of Cloisite 30B organoclay which strongly improves the melt-mixing. Secondly, water indirectly favors the bonding between PP-g-MA and the organoclay surfactant through an acid-catalyzed esterification reaction. The effect of water injection on the clay dispersion and properties improvement is however greatly superior on PP-g-MA-based nanocomposites than on PP-based nanocomposites prepared by direct melt-blending of PP, PP-g-MA and clay (one-pot process). The best clay dispersion and properties enhancement have been recorded for the PP-based nanocomposite prepared by dilution into PP of PP-g-MA-based masterbatch synthesized with water injection and high-shear rates. Water injection clearly increases the clay dispersion and consequently the nanocomposites properties. Our results point out the interest of using water-assisted extrusion for PP/clay nanocomposites elaboration. This work paves the route toward the development of water-assisted extrusion for apolar matrix-based nanocomposites.

Acknowledgments

The authors thank La Région Wallonne and FRIA (Fonds pour la formation à la Recherche dans l'Industrie et dans l'Agriculture) for financial support. J. Marchand-Brynaert is Senior Research Associate of the FRS-FNRS (Fonds National de la Recherche Scientifique, Belgium).

Appendix to Chapter 6

Scheme of the extruder equipped with the water injection system

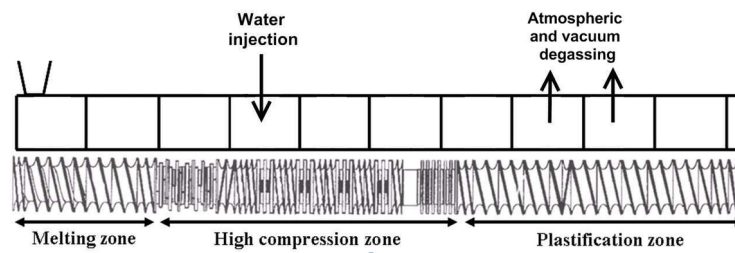


Figure 6.13: Scheme of the extruder equipped with the water injection system

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Chapter 7

Nanocomposites revisited

Ce chapitre est le bouquet final. Toutes les améliorations présentées (compatibilisant PP-g-MA optimisé, argile carboxylate et extrusion avec injection d'eau) précédemment sont combinées avec succès dans un procédé innovant "one-pot" qui peut rivaliser avec les méthodes présentées dans la littérature.

Polypropylene/clay Nanocomposites revisited

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To be submitted to Composites Science and Technology

Abstract

This work reports on an innovating one-step preparation method of polypropylene (PP)/clay nanocomposites with high degree of clay delamination and markedly improved properties (thermal, mechanical and rheological). The process is efficient for both unmodified clay and organoclay. The *in situ* synthesis of carboxylate clay and PP-graft maleic anhydride (PP-g-MA) ionomer through sodium acetate addition combined with water injection appears to be a valuable alternative to organoclay when producing PP/PP-g-MA/clay nanocomposites. The influence of PP-g-MA graft content and of its ionomer form onto the clay dispersion (native clay and organoclay) is especially investigated. Classic PP-g-MAs of low graft content are compared to a home-made highly-grafted PP-g-MA synthesized in the presence of N-bromosuccinimide (NBS). The NBS-mediated PP-g-MA, and particularly its ionomer, appear to be more efficient as compatibilizers than usual PP-g-MAs. Moreover, the nanocomposites prepared by combining the use of NBS-mediated PP-g-MA, sodium acetate and water injection exhibit the highest clay dispersion and consequently the best properties enhancements.

7.1 Introduction

The investigation of polypropylene (PP)/clay nanocomposites has received a considerable scientific and technological attention during the last decades. The main reason of this interest is the enhanced properties that are usually obtained for such polymer/clay nanocomposites

using only a few percents of clay, e.g. higher mechanical and barrier properties, flame retardant behavior whereas the material transparency can be preserved [1–4]. The wide use of PP as matrix in polymer/clay nanocomposites lies with its very large commercial importance [5]. The elaboration of PP/clay nanocomposites is especially challenging due to the huge difference of polarity between matrix and clay. These nanocomposites are traditionally prepared by melt-blending, using a compatibilizer like PP-graft-maleic anhydride (PP-g-MA) and organoclays. PP-g-MA allows the wetting of the clay surface via hydrogen-bond interactions, while the surfactants associated with organoclays (usually alkylammonium salts) increase the clay interlayer spacing and lower the clay surface energy; as a result, separation and dispersion of the clay layers into the polymer matrix are facilitated [1, 2, 6–10]. Nevertheless, the existing PP/clay nanocomposites still exhibit insufficient clay dispersion and consequently limited properties improvements are obtained. A major drawback is the poor thermal stability of the alkylammonium-surfactants which often decompose at extrusion temperatures leading to a collapse of the silicate layers [11–14] and imparting undesirable color, odor and taste to the composite [15]. Efforts have been made to synthesize more thermally stable organoclays using elaborated surfactants like pyridinium, quinolinium [16], imidazolium [17], phosphonium [18] and stibonium salts [19], but they are expensive and/or require multistep synthesis limiting large-scale productions. The usual commercial PP-g-MA compatibilizers possess low MA contents and consequently the interactions between the clay and the compatibilizers are quite limited [20]. Unfortunately, PP-g-MAs of very high MA content cannot be used since they are immiscible with PP [8, 9, 21, 22].

Recently, the N-bromosuccinimide (NBS)-mediated preparation of PP-g-MAs has been fully investigated in order to evaluate their ability to disperse the clay [20]. The use of NBS as additive during the PP-g-MA reactive extrusion synthesis allows to obtain higher [MA] graft contents while keeping acceptable molar masses [23]. When NBS-mediated PP-g-

MA/clay or PP/clay nanocomposites with NBS-mediated PP-g-MA as compatibilizer were produced, better degrees of clay delamination and dispersion as well as improved thermal stability were reached, than with classic PP-g-MAs (i.e. synthesized without addition of NBS).

Ionic functions can be introduced in polyolefins for increasing their surface energy and hence the clay dispersion and the nanocomposite properties. Enhancements of clay dispersion were reported using polyethylene (PE) ionomers (i.e. ammonium carboxylate polyampholytes prepared from polyethylene (PE)-graft-maleic anhydride, (PE-g-MA)), as matrix [24]; using poly(ethylene-co-methacrylic acid) ionomer as matrix [25–28] or as compatibilizer in PE/organoclay nanocomposites [29, 30] or in PP/organoclay nanocomposites [31, 32]. Similar improvements of clay dispersion in PP/organoclay nanocomposites were obtained using, as compatibilizer, PP-g-MA ionomer neutralized by potassium hydroxide [33, 34].

With the aim of avoiding the use of organoclays, the addition of trihydrate sodium acetate (NaAc) in the melt-compounding process for PP-g-MA/unmodified clay nanocomposites has been examined [35]. NaAc partially neutralized the maleic anhydride functions of PP-g-MA to produce *in situ* PP-g-MA ionomer [36] which simultaneously intercalated the unmodified clay [35]. This modified carboxylate clay was found thermally more stable than the usual organoclays; residual ionic groups of the partially neutralized PP-g-MA allowed favorable interactions with the clay, reinforcing the polymer/clay interface. As a consequence, the thermal and rheological properties of the nanocomposite were improved.

Recently, we applied a water-assisted extrusion process to prepare PP/clay nanocomposites [37]. Water directly increased the clay dispersion during the melt-blending step and indirectly favored the binding between PP-g-MA and the organoclay surfactant via an esterification reaction. As a result, higher degree of clay delamination and markedly improved rheological, thermal and mechanical properties were obtained.

These studies clearly pointed the need of improving the surface en-

ergy of polyolefins to enhance their ability to disperse the clay layers for the preparation of high-performance nanocomposites. In this context, the present paper discusses the elaboration of novel PP/clay nanocomposites combining the recent developments described above. For comparison, unmodified clay and organoclay are used as fillers. An optimized home-made NBS-mediated PP-g-MA is studied as compatibilizer and compared to a home-made classic PP-g-MA and to a commercial PP-g-MA. The corresponding carboxylate clays and PP-g-MA ionomers are simultaneously prepared *in situ* using trihydrate sodium acetate as additive during the melt-compounding. Lastly, the elaboration of these PP/clay nanocomposites is achieved through a water-assisted extrusion process.

7.2 Experimental

7.2.1 Materials

PP Moplen HF500N was purchased from Basell. Free radical initiator was Luperox 101 XLS 50 from Arkema (2,5-bis(tert-butyl-peroxy)-2,5-dimethylhexane (DHBP), 50 wt% blend with silica). Maleic anhydride (MA, Acros, 99 % purity), *N*-bromosuccinimide (NBS, Acros, 99 % purity) and toluene (Fisher, analytical grade) were used as received. Unmodified sodium-Montmorillonite (Cloisite Na, labeled CNa, 90.39 % in inorganic content) and sodium-Montmorillonite modified with bis(2-bis hydroxylethyl) methyl tallow ammonium chloride (Cloisite 30B, labeled C30B, 70.45 % in inorganic content) were purchased from Southern Clay Product. Trihydrate sodium acetate (NaAc) of analysis grade was purchased from Sigma-Aldrich. A commercial PP-g-MA was used for comparison: Polybond 3200 (1 wt.% of MA [manufacturer's data], labeled Plb) purchased from Chemtura.

Home-made PP-g-MAs preparation

For comparison, two home-made PP-g-MAs labeled L and H, with respectively low and high MA content, were prepared according to a known procedure [20]. A co-rotating twin-screw extruder Brabender Clam Shell TSE 20/40 was used. The extruder screw length is 800 mm with a L/D ratio of 40. The barrel temperature is fixed at 200 °C, the screw speed is set to 40 RPM and the throughput is around 2 kg/h, which allowed a residence time of about 1 minute. The extruded samples were immediately quenched into cold water and cryo-ground. PP-g-MA L was synthesized via the classic route, using 5 wt.% of MA, 0.45 wt.% of DHBP and PP-g-MA H, using 5 wt.% of MA, 0.45 wt.% of DHBP and 0.09 wt.% of NBS.

Nanocomposites preparation

References (samples without clay) and nanocomposites were prepared in a co-rotating twin-screw extruder Krupp WP ZSK25. The composition of the nanocomposites and the corresponding references are given in Table 7.1 when Plb is used as compatibilizers, and in Table 7.2 when PP-g-MA L and H are the home-made compatibilizers. The extruder screw length is 1000 mm with a L/D ratio of 40 and the barrel temperature is fixed at 200 °C. Water, when used, was pumped at a rate of 5.7 wt% into the extruder in the high compression zone. The special design of the screw allows the pressure to increase up to 125 bars in this zone which maintains the water liquid [37, 38]. The water is degassed in the transport zone and fully removed using a vacuum pump. All samples were extruded at a screw speed of 200 RPM¹ and a throughput of 7 kg/h. The extruded samples were immediately quenched into cold water and pelletized. CNa and CN30B have an inorganic content of 90.39 % and 70.45 %. Thus to reach 5 wt.% of clay inorganic content in the resulting nanocomposite, 5.5 wt.% (rounded at 6 wt.%) of CNa

¹A screw speed of 200 RPM instead of 1000 RPM was chosen to stay in industrial conditions

or 7.1 wt.% (rounded at 7 wt.%) of C30B are required (Tables 7.1 and 7.2). The amounts of NaAc used here are 2 or 4 wt.%, corresponding to 2.8 and 5.5 equivalents of the cation exchange capacity of CNa (0.920 meq./g).

After extrusion, all samples were injection-molded using a Krauss-Maffei type KM 80-160E injection molding machine into standard dog-bone specimens (ASTM 527). The barrel temperatures ranged within 170-200 °C and the mold temperature was kept at 25 °C. Before injection-molding, pelletized samples were dried for 24h at 70 °C under vacuum. All characterizations were realized on injection-molded samples.

Encoding of samples

PP Y (x)N / Z (W) (Tables 7.1 and 7.2). PP = polypropylene matrix for all samples. Y = compatibilizer; Y = P for Plb; Y = L for home-made PP-g-MA with low MA content; Y = H for home-made PP-g-MA with high MA content. xN = wt.% of NaAc; x = 2 or 4 (when not mentioned, it means 4). Z = clay; Z = A for CNa (native clay); Z = B for C30B (organomodified clay). W = water-assisted process, indicated by W when applied.

7.2.2 Characterizations

Transmission electron microscopy (TEM). Samples were ultramicrotomed at ambient temperature with a Reichert Microtome and collected on a 300 mesh copper grid. TEM pictures were recorded with a LEO 922 microscope operating at 200 kV.

X-ray diffraction (XRD). The clay interlayer spacing of the nanocomposites was measured by XRD on a Bruker D8 Advance diffractometer using $\text{CuK}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) at 40 kV and 30 mA.

Fourier Transform Infrared (FTIR) spectroscopy. FTIR spectra were recorded on a Nicolet Nexus 870 FTIR spectrometer on compression-molded films in transmission mode by cumulating 16 scans at a resolution of 4 cm^{-1} over a spectral range from 4000 to 400 cm^{-1} . Films

Table 7.1: Composition of the references and nanocomposites using Plb (P) as compatibilizer.

Samples	PP-g-MA	Clay	PP (wt%)	PP-g-MA (wt%)	NaAc (wt%)	Clay (wt%)	Water
PPP	P	/	90	10	0	0	/
PPP/A	P	CNa	85	9	0	6	/
PPP/AW	P	CNa	85	9	0	6	yes
PPP2N	P	/	88	10	2	0	/
PPP2N/A	P	CNa	83	9	2	6	/
PPP2N/AW	P	CNa	83	9	2	6	yes
PPP4N	P	/	86	10	4	0	/
PPP4N/A	P	CNa	81	9	4	6	/
PPP4N/AW	P	CNa	81	9	4	6	yes

Table 7.2: Composition of the references and nanocomposites using PP-g-MA (L) or PP-g-MA (H) as compatibilizers.

Samples	PP-g-MA	Clay	PP (wt%)	PP-g-MA (wt%)	NaAc (wt%)	Clay (wt%)	Water
PPL	L	/	90	10	0	0	/
PPL/A	L	CNa	85	9	0	6	/
PPL/AW	L	CNa	85	9	0	6	yes
PPL/B	L	C30B	84	9	0	7	/
PPL/BW	L	C30B	84	9	0	7	yes
PPLN	L	/	86	10	4	0	/
PPLN/A	L	CNa	81	9	4	6	/
PPLN/AW	L	CNa	81	9	4	6	yes
PPLN/B	L	C30B	80	9	4	7	/
PPLN/BW	L	C30B	80	9	4	7	yes
PPH	H	/	90	10	0	0	/
PPH/A	H	CNa	85	9	0	6	/
PPH/AW	H	CNa	85	9	0	6	yes
PPH/B	H	C30B	84	9	0	7	/
PPH/BW	H	C30B	84	9	0	7	yes
PPHN	H	/	86	10	4	0	/
PPHN/A	H	CNa	81	9	4	6	/
PPHN/AW	H	CNa	81	9	4	6	yes
PPHN/B	H	C30B	80	9	4	7	/
PPHN/BW	H	C30B	80	9	4	7	yes

were obtained by compression-molding of one head of the injection-molded dog-bone specimens. The spectra of PP/clay references and nanocomposites were normalized by setting the peak height of the 2723 cm^{-1} absorption band (characteristic C-H stretching of PP) to an absorbance of 1.

Thermogravimetric analysis (TGA). The thermal stability of the references and composites was studied by TGA. The analyses were performed on a Mettler Toledo TGA/SDTA 851e using a heating rate of $20\text{ }^{\circ}\text{C}/\text{min}$ under air or nitrogen atmosphere ($100\text{ ml}/\text{min}$) from 25 to $1000\text{ }^{\circ}\text{C}$. The temperatures at 5% (T-5) weight loss under air atmosphere are determined and each value is the average of minimum 3 experiments.

Rheology. Rheological measurements were carried out in an oscillatory mode on a Bohlin Gemini II rheometer equipped with a parallel plate geometry using 25 mm diameter plates. Frequency sweep tests were performed on compression-molded samples of about 1.0 mm in thickness at a strain rate of 10 % for references and nanocomposites. Testing temperature was $180\text{ }^{\circ}\text{C}$ for PP-g-MA/clay nanocomposites and $200\text{ }^{\circ}\text{C}$ for PP/clay nanocomposites. Experimental conditions were preliminary adjusted to work in the linear viscoelastic range.

Mechanical testing. Tensile tests were performed on a Zwick tensile machine using a 50 kN force sensor and an extensometer for strain measurement. Tests were conducted at a crosshead speed of $5\text{ mm}/\text{min}$ for Young's modulus measurement. Presented results are averaged on three experiments.

7.3 Results and Discussion

PP/PP-g-MA/unmodified clay nanocomposites produced by synthesizing *in situ* carboxylate clay and PP-g-MA ionomer with and without water injection were firstly examined. PP/CNa composites were prepared by direct melt-blending of PP, PP-g-MA, NaAc and CNa (Table 7.1). The PP-g-MA used as compatibilizer is a commercial one

Table 7.3: Characterization of PP and home-made PP-g-MAs. [MA] is the concentration of grafted maleic anhydride, Xc is the crystallinity degree and Mn and Mw are the number and weight average molar masses.

Samples	[MA] (wt%)	Xc (%)	Mn (kg/mol)	Mw (kg/mol)
PP	/	48	46	220
Plb	0.4	47	25	72
L	0.5	47	24	90
H	1.2	40	12	33

(Plb) of low-MA content. The amount of NaAc is crucial as mentioned in the previous work [35]. NaAc is consumed to intercalate CNa and to partially neutralize PP-g-MA into ionomer; 2 and 4 wt.% NaAc were examined.

Moreover, NBS-mediated PP-g-MAs were shown to be more efficient as matrix than classic PP-g-MA when producing model PP-g-MA/organoclay nanocomposites [20]. In order to study the efficiency onto clay dispersion of such compatibilizers and of their ionomers, PP/PP-g-MA/clay nanocomposites with and without NaAc, were prepared by direct melt blending with and without the help of water injection. An optimized home-made NBS-mediated PP-g-MA of high-MA content (PP-g-MA H) is compared to a corresponding home-made classic PP-g-MA (PP-g-MA L). Two clays are used, an unmodified clay (CNa) and an organoclay (C30B) (Table 7.2).

7.3.1 Characterizations of the home-made PP-g-MAs

The synthesis of PP-g-MA L and H was described in a previous work [20]. The conditions (with NBS) allow to reach higher MA content than usual classic PP-g-MAs (without NBS) while maintaining acceptable molar masses. The MA content ([MA]), the crystallinity degree (Xc) and the molar masses (Mn and Mw) are presented in Table 7.3 and compared to those of Plb. The graft content and molar masses of PP-g-MA L are quite comparable to Plb while PP-g-MA H has a graft

content more than twice higher than PP-g-MA L.

7.3.2 Morphological and structural characterizations of the PP/clay nanocomposites

The nanocomposites are characterized by XRD to follow the changes of the clay basal spacing and by TEM to examine their clay dispersion. The neutralization of PP-g-MA into an ionomer by sodium acetate is monitored by FTIR.

Figure 7.1 shows the XRD patterns of PP/CNa composites using, as compatibilizers, Plb, PP-g-MA L or PP-g-MA H. The unmodified clay (CNa) presents only one reflexion centered at 1.24 nm ($7.1^\circ 2\theta$), which corresponds to the presence of one layer of water in the clay interlayer [39, 40].

PP/CNa composites prepared without NaAc all exhibit a decrease of their clay basal spacing (from 1.24 nm to 0.99 nm ($8.9^\circ 2\theta$) for samples using Plb as compatibilizer (PPP/A, PPP/AW) and to around 1.2 nm ($7.3\text{--}7.5^\circ 2\theta$) for samples using PP-g-MA L (PPL/A, PPL/AW) or H (PPH/A, PPH/AW) as compatibilizer). This decrease of basal spacing corresponds to a partial loss of the interlayer water since the value for completely dehydrated clay is of 0.97 nm ($9.1^\circ 2\theta$). The PP/CNa composites prepared with NaAc show an increase of their clay basal spacing from 1.24 nm ($7.1^\circ 2\theta$) to 2.01 nm ($4.4^\circ 2\theta$), whatever the compatibilizer employed (PPP2N/A, PPP4N/A, PPLN/A and PPHN/A). This increase is attributed to NaAc intercalation between the clay interlayer [35].

PP/CNa composites prepared with 2 wt.% of NaAc with and without water injection (PPP2N/A and PPP2N/AW, respectively), exhibit a broad peak around 1.05 nm ($8.4^\circ 2\theta$) corresponding to partially dehydrated clay and a slight overlapping reflexion at $8.8^\circ 2\theta$ is noticed for the one prepared with water injection (PPP2N/AW). The peak at $8.8^\circ 2\theta$ is attributed to the (010) reflexion of NaAc [35]. Other PP/CNa

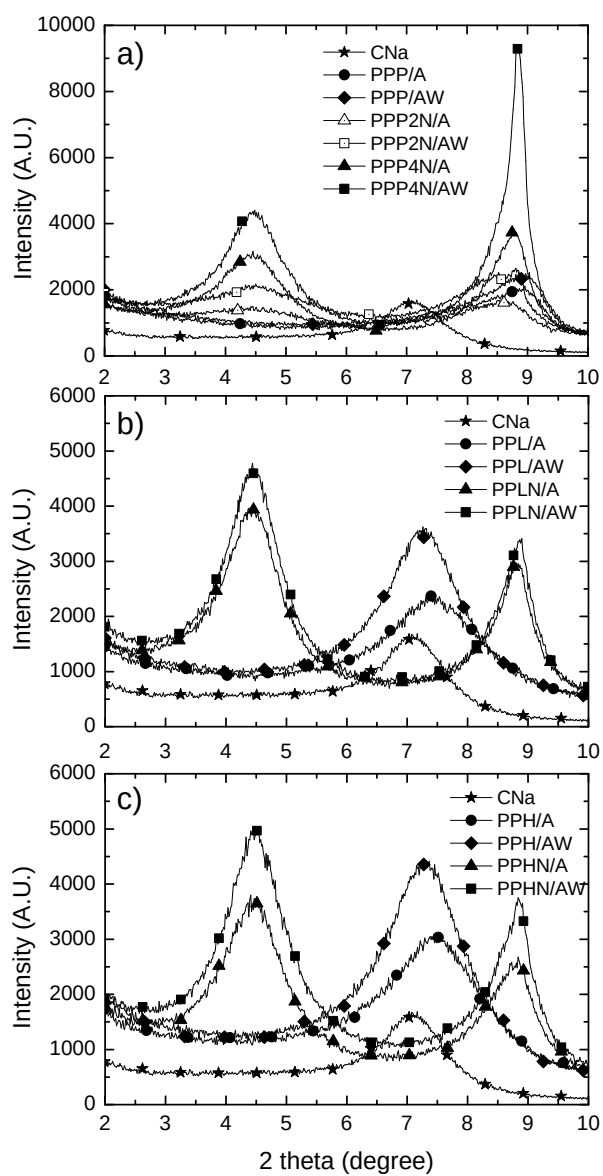


Figure 7.1: XRD patterns of PP/CNa composites using, as compatibilizers, a) Plb, b) PP-g-MA L and c) PP-g-MA H.

composites prepared with 4 wt.% of NaAc (PPP4N/A, PPP4N/AW, PPLN/A, PPLN/AW, PPHN/A and PPHN/AW) show only the NaAc reflexion. The appearance of the (010) NaAc reflexion corresponds to a part of NaAc not intercalated assuming that crystalline NaAc is excluded from the silicate layers [35]. Therefore, at 2 wt.%, NaAc seems totally consumed to intercalate part of the clay and the rest of the clay is dehydrated. At 4 wt.% of NaAc, it seems that all the clay is intercalated by NaAc with an excess of free NaAc. It is however impossible to confirm the absence of dehydrated clay in those last samples since the corresponding reflexion is totally overlapped by the (010) one of NaAc.

Figure 7.2 shows the XRD patterns PP/C30B nanocomposites using PP-g-MA L or PP-g-MA H as compatibilizers. The C30B clay possesses a basal spacing centered at 1.88 nm ($4.7^\circ 2\theta$). All PP/C30B nanocomposites exhibit their main basal spacing at 1.45 nm ($6.1^\circ 2\theta$), except for PPLN/B which shows a broad peak around 1.58 nm ($5.6^\circ 2\theta$). The shift of basal spacing to higher diffraction angles, indicates that a part of the C30B silicate layers has collapsed. This results from the C30B surfactant degradation, as already observed by other authors [37, 41, 42].

The second basal spacing visible at $2.5 - 3^\circ 2\theta$ for PPL/B and at 2.39 nm ($3.7^\circ 2\theta$) for PPL/BW and PPH/BW, indicates that another part of the C30B silicate layers has been intercalated. Except PPL/B and PPL/BW, the PP/C30B materials show an increase of their diffraction intensity in the low angle region which is commonly attributed to completely dispersed clay layers [8, 43]. Better clay dispersion is then expected for PP/C30B blends prepared using water injection and PP-g-MA H than using PP-g-MA L.

PP/C30B mixtures prepared with NaAc (PPLN/B, PPLN/BW, PPHN/B and PPHN/BW) exhibit a more pronounced increase of their diffraction intensity toward low angles, sign of a higher degree of clay delamination, but also an intense (010) NaAc reflexion indicating that NaAc does not intercalate C30B as it does with CNa.

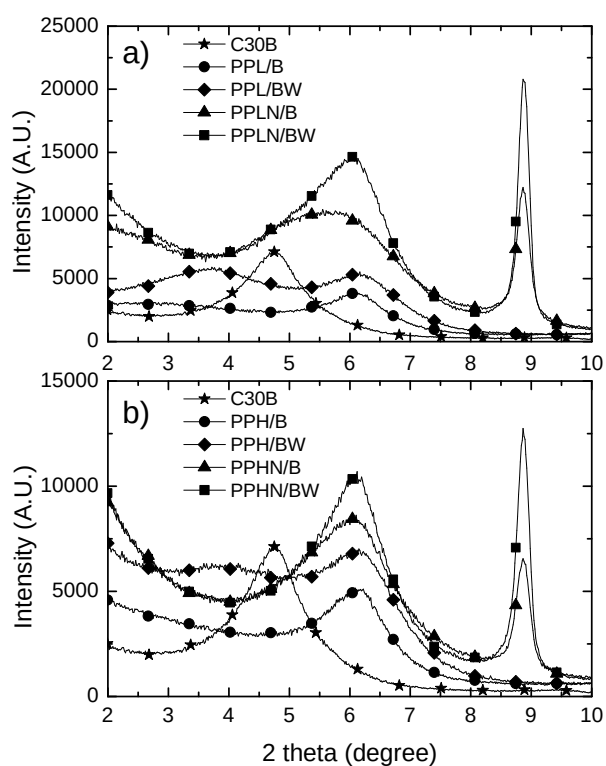


Figure 7.2: XRD patterns of PP/C30B nanocomposites using, as compatibilizers: a) PP-g-MA L and b) PP-g-MA H.

Figure 7.3 shows FTIR spectra in the carbonyl region of PP/clay references and nanocomposites using as compatibilizer, Plb, PP-g-MA L or PP-g-MA H. Since the spectra were normalized, they can be compared semi-quantitatively. The spectra of PP/clay samples prepared without NaAc are not displayed since they are similar to their respective PP/PP-g-MA blends.

Three main absorption bands can be observed in the $1450\text{--}1800\text{ cm}^{-1}$ region : (1) the maleic anhydride band (carbonyl symmetric stretching) around $1780\text{--}1790\text{ cm}^{-1}$; (2) the carboxylic acid band (carbonyl stretching) around 1710 cm^{-1} and (3) the carboxylate band (carbonyl asymmetric stretching) around $1560\text{--}1580\text{ cm}^{-1}$. The region of the two first bands is enlarged on the insets in Figure 7.3.

All samples containing NaAc exhibit a significant reduction of their anhydride band in comparison to the corresponding PP/PP-g-MA blends (see the insets in Figure 7.3(a), (b) and (c)). The anhydride band diminution is due to the neutralization of PP-g-MA into ionomer by NaAc.

The appearance of the carboxylate band for these samples arises mainly from NaAc itself. The contribution of the carboxylate product of the neutralization (similar in intensity to the anhydride and acid bands [36]), can be neglected.

The carbonyl asymmetric stretching of pure NaAc (ionic solid) is measured at 1570 cm^{-1} (spectrum not shown). The carboxylate band of the PP/PP-g-MA blends containing NaAc is measured at 1580 cm^{-1} while the one of the PP/CNa composites prepared with NaAc is measured at 1560 cm^{-1} . The high-frequency shift in the first case probably results from ionic cluster strengthening due to intermolecular interactions [33]. The low-frequency shift in the second case corresponds to a change of the carboxylate coordination which becomes of bridging-type when NaAc is intercalated into CNa [35]. The carboxylate band of PP/CNa composites containing 4 wt.% of NaAc, displays a shoulder

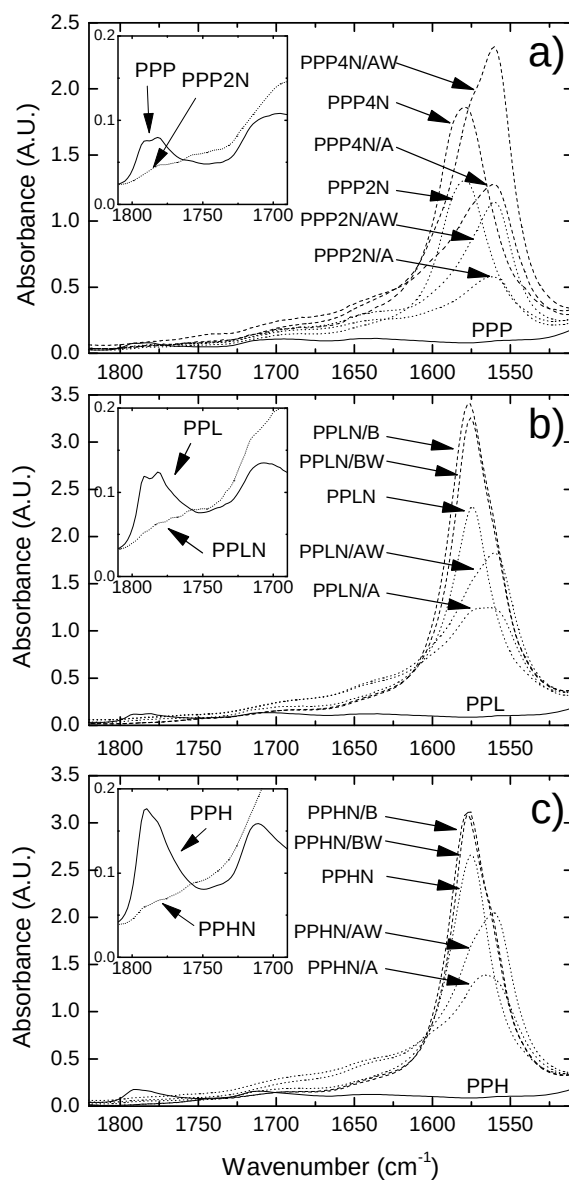


Figure 7.3: FTIR patterns of PP/clay references and nanocomposites using, as compatibilizer: a) Plb, b) PP-g-MA L and c) PP-g-MA H.

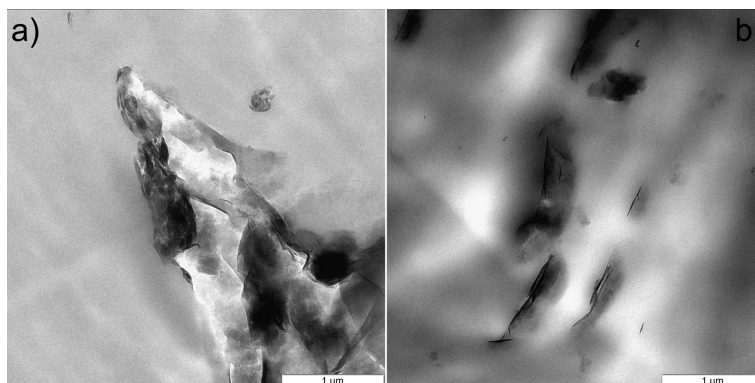


Figure 7.4: TEM pictures of PP/CNa composites: a) PPP/A; b) PPHN/AW.

around 1575 cm^{-1} attributed to NaAc in excess which is not intercalated into the clay, nor consumed to neutralize PP-g-MA. This agrees with the XRD patterns showing an intense (010) NaAc reflexion.

PP/C30B nanocomposites present their carboxylate band at the same wavenumber than the corresponding PP/PP-g-MA blends containing NaAc, which confirms that NaAc does not intercalate C30B, in accordance with the XRD results.

The morphology of PP/CNa composites has been examined by TEM microscopy (full data not shown). All samples exhibit similar heterogeneous clay dispersion with large clay aggregates of several microns (PPP/A, PPL/A and PPH/A). The use of water injection slightly raises the clay dispersion; a mixture of large and small clay aggregates is observed (PPP/AW, PPL/AW and PPH/AW). The combined use of water injection and NaAc leads to a fine clay dispersion, composed of small clay stacks only (PPP4N/AW, PPLN/AW and PPHN/AW). The best clay dispersion among PP/CNa composites is observed when PP-g-MA compatibilizer with high MA-content is used; the sample exhibits small clay stacks and individual clay layers (PPHN/AW). Figures 7.4a and 7.4b illustrate TEM pictures of PPP/A compared to PPHN/AW show-

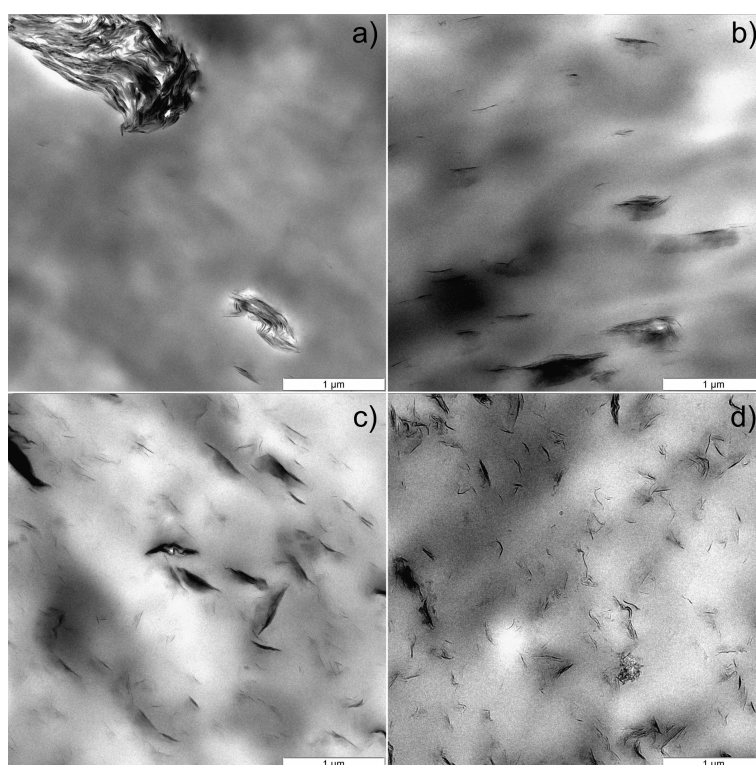


Figure 7.5: TEM pictures of PP/C30B nanocomposites: a) PPL/B; b) PPH/B; c) PPLN/BW; d) PPHN/BW.

ing significant exfoliation improvement.

Figure 7.5 gives TEM pictures of PP/C30B nanocomposites. PPL/B shows large clay aggregates (Figure 7.5a). Increasing the MA content of PP-g-MA allows to obtain materials with a mixed distribution of exfoliated clay layers and small clay aggregates (PPH/B, Figure 7.5b). Water injection slightly improves the dispersion (not shown).

PP/C30B nanocomposites prepared with NaAc exhibit a much better clay delamination degree than in the absence of NaAc. A mixture of small clay stacks and some individualized clay layers, in place of large clay aggregates, is visible when using the compatibilizer of low-MA content (PPLN/B). Water injection further allows to distribute homogeneously the filler (PPLN/BW, Figure 7.5c). Homogeneously-distributed, well-individualized clay layers and a few clay stacks are obtained with PP-g-MA of high-MA content as compatibilizer. Lastly, the highest density of individualized clay layers distribution is recovered when water is injected during the process (PPHN/BW, Figure 7.5d). Thus, the use of PP-g-MA H, water injection and NaAc, and especially their combination, markedly improves the C30B dispersion.

7.3.3 Thermal, rheological and mechanical characterizations of the PP/clay nanocomposites

Higher thermal stability is commonly observed when clay platelets are well-dispersed into the polymer matrix, as a result of hindered out-diffusion of the volatile decomposition products and also of char formation acting as a physical barrier between the polymer and the oxidative medium [1]. In thermogravimetric analysis, the temperature at 5% weight loss (T-5) is usually considered as the initial decomposition temperature [43], and can be used to evaluate and compare the thermal stability of samples. TGA results are here presented as T-5 difference ($\Delta T-5$) between the studied nanocomposite and its corresponding PP/PP-g-MA blend.

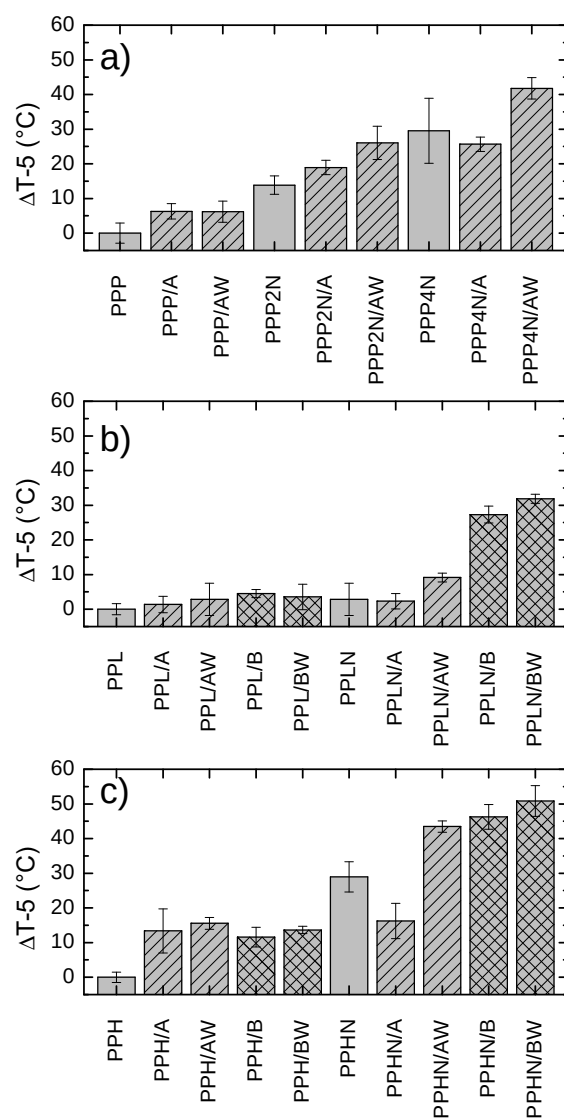


Figure 7.6: TGA results of PP/clay references and nanocomposites using, as compatibilizer, a) PPl, b) PP-g-MA L and c) PP-g-MA H.

Figure 7.6 summarizes the TGA results for PP/clay references and nanocomposites using the different compatibilizers, Plb, PP-g-MA L and PP-g-MA H.

There are no important differences of thermal stability among PP/clay composites prepared without NaAc, whatever the clay or the compatibilizer employed. They all show a slight increase of $\Delta T-5$ in comparison to their respective PP/PP-g-MA blends, consistently with their poor clay dispersion. Such weak thermal stability improvements are comparable to those previously reported for PP/CNa microcomposites [44] and for Plb/CNa microcomposites [37].

Except for PP-g-MA L, significant raise of $\Delta T-5$ is observed for PP/PP-g-MA blends when adding NaAc. The doubling of NaAc amount in PP/Plb blends (PPP, PPP2N, PPP4N) leads to a significant further increase of $\Delta T-5$. Similar improvements of thermal stability were reported for PP-g-MA ionomers [36] and attributed to the aggregation of the carboxylate moieties into ionic clusters. The fact that NaAc does not modify the thermal stability of PP/PP-g-MA L blend (PPL versus PPLN), could be explained by residual unreacted MA still present. Indeed, when free MA is neutralized by NaAc, the resulting carboxylate moieties do not affect any polymer chain.

However, the addition of NaAc combined with water injection, improves the thermal stability of all the PP/CNa composites.

For PP/C30B nanocomposites, the addition of NaAc leads to strong thermal stability improvements which are further enhanced with water injection. Whatever the clay or the compatibilizer employed, the combination of NaAc and water injection gives the best thermal stability increase; moreover, higher thermal stabilities can be reached with C30B as filler than with CNa, and using PP-g-MA H as compatibilizer rather than PP-g-MA L or Plb. The excellent results recorded for PPHN/AW and for PPHN/BW (Figure 7.6c) are directly correlated to their high clay delamination degree. However, a higher degree of clay delamination is observed using C30B rather than CNa. The unexpected almost

equivalent thermal stability in the case of CNa, could be explained by the fact that native clay could furthermore adsorb part of the decomposition products, delaying the weight loss of the sample.

Rheological characterization is used to evaluate the dispersion state of the filler. Indeed, the melt flow behavior is quite sensitive to the structure, particle size and shape, and surface properties of a dispersed phase [45, 46]. When adding fillers to a polymer matrix, favorable filler-matrix interactions are created and an increase of the elastic modulus (G') and of the complex viscosity (η^*) at low frequencies is observed. If a percolating mesoscopic filler network is formed, an elastic modulus plateau most often appears and the complex viscosity continuously raises at low frequencies.

Figure 7.7 shows the G' and η^* curves of PP/CNa references and nanocomposites using Plb, PP-g-MA L or PP-g-MA H as compatibilizers, insofar as they differ.

There are no important differences of rheological properties among PP/CNa composites prepared without NaAc, whatever the compatibilizer employed; they all exhibit a typical liquid-like behavior (at low frequencies, G' has a slope close to 2 and η^* reaches a Newtonian plateau). Their small increase of properties in comparison with the corresponding PP/PP-g-MA blends, is in agreement with their poor clay dispersion. The enhancement of G' and η^* noticed for PP/PP-g-MA blends when adding NaAc results from the higher viscoelastic properties of the *in situ* formed PP-g-MA ionomers.

PP/CNa composites prepared with and without water, using Plb and 2 wt.% of NaAc (PPP2N/A and PPP2N/AW) or using PP-g-MA L and NaAc (PPLN/A and PPLN/AW), show similar slight increase of G' and η^* than the respective PP/CNa composites without NaAc. Samples prepared using Plb (PPP4N/A and PPP4N/AW) or using PP-g-MA H (PPHN/A and PPHN/AW) exhibit an additional increase of G' and η^* in comparison with their corresponding PP/PP-g-MA blends

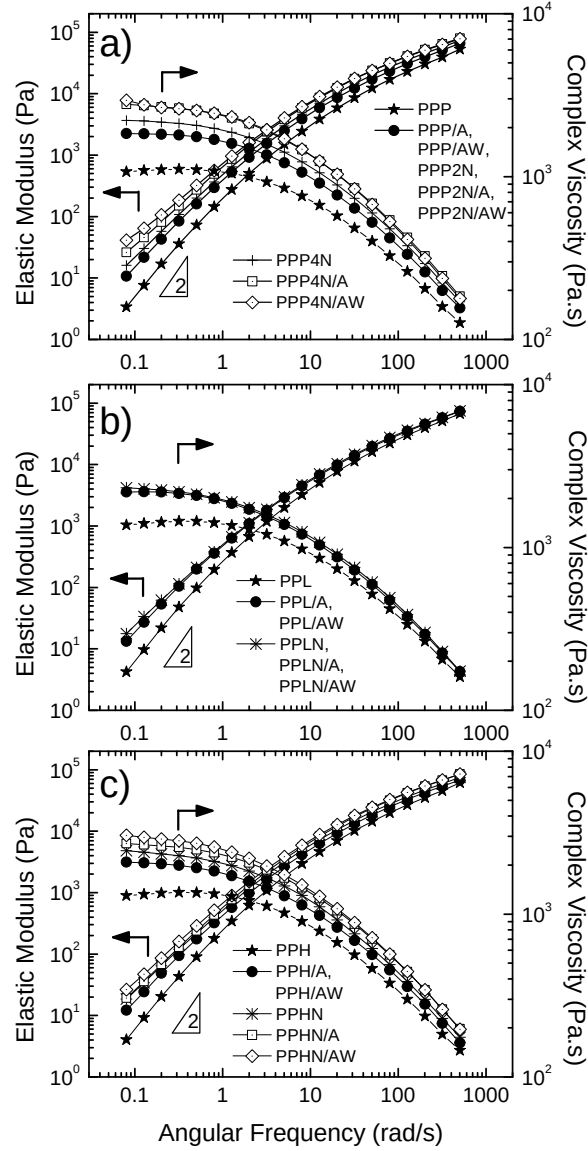


Figure 7.7: Rheological measurements of PP/CNa references and nanocomposites using, as compatibilizer, a) Plb, b) PP-g-MA L and c) PP-g-MA H.

with NaAc (PPP4N and PPHN), and much more pronounced at low frequency when using water injection (PPP4N/AW and PPHN/AW).

The observed rheological improvements could be explained by a matrix reinforcement due, on the one hand, to the link between clay and polymer matrix by both hydrogen-bond and strong ionic interactions, and on the other hand, to the ionic aggregation of the carboxylate moieties. Without water injection, the materials (PPP4N/A, PPLN/A and PPHN/A) present a poor clay dispersion and consequently a matrix reinforcement mainly due to ionic aggregation is more probable.

The similarity of rheological properties for PP/CNa composites using PP-g-MA L (Figure 7.6(b)) may have its origin in the presence of free unreacted MA into PP-g-MA L, as already invoked.

The combination of water injection and NaAc addition thus markedly increases the rheological properties of PP/CNa composites, confirming the previous TGA results.

Figure 7.8 shows the G' and η^* curves of PP/C30B references and nanocomposites using PP-g-MA L or PP-g-MA H as compatibilizer. Without NaAc, PP/C30B nanocomposites show similar G' and η^* curves to PP/CNa composites, featuring a typical liquid-like behavior. The addition of NaAc to PP/C30B nanocomposites dramatically increases G' and η^* curves, and water injection further leads to the highest increase of G' and η^* curves at low frequency associated to a decrease of the G' frequency dependence and a loss of the η^* plateau, meaning that C30B platelets and tethered molecules form a three-dimensional structure. The higher matrix reinforcement is obtained using our home-made PP-g-MA H as compatibilizer. Rheological characterizations confirm the previous observations, i.e. the interest to use PP-g-MA H, water injection and NaAc in a one-pot process.

Mechanical reinforcement is expected when clay platelets are well-dispersed into the polymer matrix. Especially, Young's modulus commonly increases when the filler dispersion and the interfacial interactions

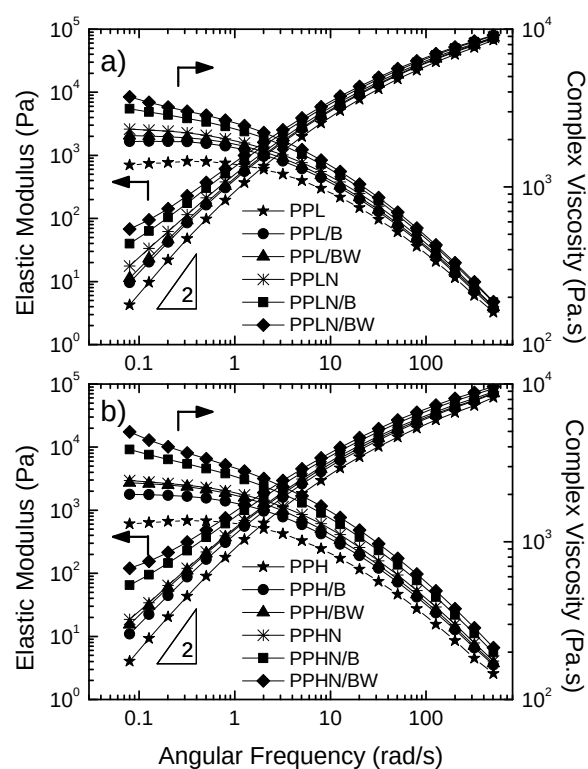


Figure 7.8: Rheological measurements of PP/C30B references and nanocomposites using, as compatibilizers, a) PP-g-MA L or b) PP-g-MA H.

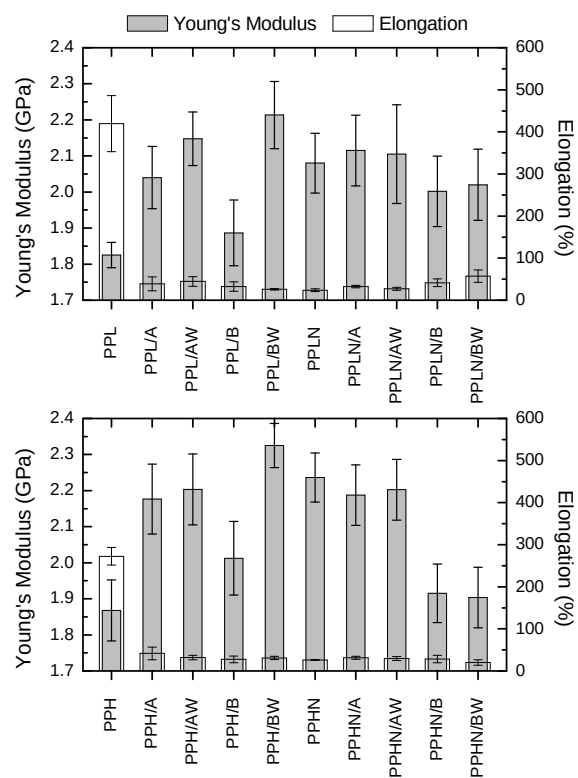


Figure 7.9: Mechanical testing measurements of PP/clay references and nanocomposites using, as compatibilizers, a) PP-g-MA L or b) PP-g-MA H.

are improved. Indeed, enlarging the interface between the matrix and the filler increases the volume of polymer chains influenced by the rigid clay platelets. Figure 7.9 shows the relative Young's modulus (E') and the elongation from tensile tests of PP/clay reference and nanocomposites using PP-g-MA L or PP-g-MA H as compatibilizers.

The addition of clay (CNa or C30B) increases the E' of PP/PP-g-MA blends of about 15–20 %. For PP/CNa composites, water injection and/or NaAc addition do not significantly change further E' . The addition of C30B without water and without NaAc leads to lower reinforcement than using CNa. Water injection combined with the addition of C30B gives the best enhancement of mechanical properties (increase of E' of about 20–25 %). Surprisingly, PP/C30B nanocomposites prepared using NaAc with or without water injection exhibit an important reduction of E' . This observation is neither consistent with their high clay delamination degree, nor with their enhanced thermal and rheological properties. One can suppose that the excess of NaAc in PP/C30B nanocomposites is responsible of their lower Young's modulus.

Globally, PP/clay nanocomposites prepared with PP-g-MA H as compatibilizer lead to higher reinforcement than using PP-g-MA L. This definitively confirms that NBS-mediated PP-g-MA having high-MA content is more efficient as compatibilizer than the classic ones. PP-g-MA of high-MA content forms a lot of links between the clay and the polymer which improve the interfacial interactions.

PP/clay nanocomposites break at lower elongation rates (around 25–45 %) than their corresponding PP/PP-g-MA blends (Figure 7.9). The mineral fillers such as layered silicates, are indeed well known to decrease the ductility of the polymers [4].

7.4 Conclusions

PP/clay nanocomposites with a high level of clay delamination and significant properties improvement have been successfully obtained by a

novel one-step preparation method. The *in situ* synthesis of carboxylate clay and PP-g-MA ionomer through sodium acetate addition and with the help of water injection was found to be an effective alternative to organoclays for the elaboration of PP/clay nanocomposites. When dispersing unmodified clay into a PP/PP-g-MA blend, only very large clay aggregates are formed and the properties enhancement remains very modest. By adding 4 wt.% of trihydrate sodium acetate and by using a water-assisted extrusion process, we successfully produced composites showing a finer clay dispersion and enhanced thermal, rheological and mechanical properties. These results demonstrate the feasibility of PP/clay composites from unmodified clay.

NBS-mediated PP-g-MA containing higher grafting level than classic PP-g-MA was then used for the elaboration of PP/clay nanocomposites based on the the aforementioned process, from both unmodified clay and organoclay. Whatever the clay and the compatibilizer employed, the combination of water injection and sodium acetate addition always brought strong improvements of clay dispersion and properties enhancement. However, the NBS-mediated PP-g-MA, and even more its ionomer, revealed to be much more effective as compatibilizer than the classic PP-g-MA and its ionomer. Particularly, the combined use of NBS-mediated PP-g-MA, sodium acetate, organoclay and water injection led to the highest degree of clay delamination and the greatest enhancement of thermal and rheological properties. Interestingly, our innovating one-step process worked as well with the less expensive native clay.

Acknowledgments

The authors thank La Région Wallonne and FRIA (Fonds pour la formation à la Recherche dans l'Industrie et dans l'Agriculture) for financial support. J. Marchand-Brynaert is Senior Research Associate of the FRS-FNRS (Fonds National de la Recherche Scientifique, Belgium).

Prof. J. Devaux and Prof C. Bailly (Université catholique de Louvain, UCL) are acknowledged for useful discussions and advices.

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Chapter 8

Conclusions and Prospects

General Conclusions

Despite extensive researches during the last decades, polypropylene (PP)/clay nanocomposites still show limited properties enhancement which clearly restrains their industrial development. The two main reasons of their limited properties are the poor thermal stability of the alkyl-ammonium- surfactants in the organoclay and the low graft content of PP-graft maleic anhydride (PP-g-MA) used as compatibilizer. Moreover, the dispersion mechanisms of the clay into the polymer matrix (intercalation and exfoliation) are currently not well understood. The global objective of the thesis was the optimization of polypropylene/clay nanocomposites by resolving or finding alternatives to the aforementioned limitations.

A large part of this thesis was devoted to the study and the optimization of functionalized PPs as compatibilizers. Firstly, we focused on the synthesis and characterization of new PP ionomers based on elastomeric highly functionalized PP-g-MAs. We developed a method based on infrared spectroscopy to quantify the effective neutralization degree of the PP-g-MA ionomers. One of the key points of the neutralization process is that water is required to ionize the base and to allow the acid-base reaction to occur. Trihydrate sodium acetate was preferred as base since it is a powdered solid that contains crystallization water and melts before the PP-g-MA. Furthermore, it does not lead to corrosion and its reaction residue is evaporated during the ionomer synthesis. The physical properties of the resulting ionomers were strongly improved, especially their thermal stability and rheological properties were largely increased as a function of the neutralization degree.

The elastomeric highly functionalized PP-g-MAs aforementioned were prepared by adding large amounts of N-bromosuccinimide (NBS) during the reactive extrusion process. They possess very high MA contents, high molar masses but exhibit no crystallinity and unfortunately,

they are immiscible with PP. In view to optimize the PP-g-MA synthesis for the preparation of model PP-g-MA/clay nanocomposites and PP/clay nanocomposites, new NBS-mediated PP-g-MAs were prepared by adapting the amount of NBS during the synthesis. As a result, the new NBS-mediated PP-g-MAs prepared with low amounts of NBS, have significantly higher graft content than classic PP-g-MAs prepared without NBS while they keep acceptable molar masses and present almost no drop of crystallinity. Moreover, they are miscible with PP.

Globally, much better clay dispersions and thermal properties were reached for PP-g-MA/clay nanocomposites prepared using NBS-mediated PP-g-MAs than using the corresponding PP-g-MAs synthesized without NBS. The increase of PP-g-MA graft content clearly raises the clay exfoliation degree while an important reduction of the PP-g-MA crystallinity leads to a poor clay dispersion. It was also shown that, within the examined range of molar masses, the PP-g-MA molar mass has no influence on the clay dispersion. Based on these results, an “optimized” NBS-mediated PP-g-MA sample was selected. The resulting PP/clay nanocomposite prepared using the latter as compatibilizer shows much better clay dispersion and thermal stability than the one prepared using a corresponding classic PP-g-MA.

In view to examine alternatives to alkylammonium clays when producing PP/clay nanocomposites, the synthesis and characterization of carboxylate clays was fully investigated. Carboxylate clays are easily prepared into methanol from unmodified clay and preferentially using anhydrous sodium acetate as carboxylate salt. The resulting carboxylate clay is more thermally stable than a classical alkylammonium clay and does not degrade at extrusion temperature. PP-g-MA/carboxylate clay composites show better clay dispersion and properties than PP-g-MA/unmodified clay. It was found that intercalated sodium acetate neutralizes the anhydride/acid functions of PP-g-MA during the compounding with the carboxylate clay.

The best improvements of clay dispersion and properties enhancements were obtained when preparing PP-g-MA/carboxylate clay nanocomposites via a one-pot process: the carboxylate clay is synthesized *in situ* during the compounding of PP-g-MA in presence of unmodified clay and trihydrate sodium acetate. Trihydrate sodium acetate which is melted at extrusion temperature, intercalates the unmodified clay and neutralizes PP-g-MA into ionomer *in situ*. A strong synergy effect of the clay and the trihydrate sodium acetate was clearly demonstrated. The properties enhancements can be explained by a matrix reinforcement due to the clay linked to the polymer by both hydrogen-bond and strong ionic interactions even if a reinforcement due to the ionic aggregation of the carboxylate moieties cannot be totally excluded.

The clay delamination degree and the performances of polyamide/unmodified clay nanocomposites are strongly improved when prepared with water injected under pressure directly into the melt blend. Following this concept, the elaboration of PP/(organo)clay nanocomposites was investigated with and without the help of water injection and/or high-shear rates. The combined use of water injection and high-shear rates showed a remarkable synergy effect in increasing the organoclay exfoliation into a PP-g-MA matrix. It was shown that an esterification reaction occurred between the hydroxyl functions of organoclay surfactant and carboxylic acids of PP-g-MA resulting from the anhydride hydrolysis. The effect of water injection on the clay dispersion and properties improvement is however greatly superior on PP-g-MA-based nanocomposites than on PP-based nanocomposites prepared by direct melt-blending of PP, PP-g-MA and clay. For PP-based nanocomposites, the best clay delamination degree and properties enhancement have been reached by dilution into PP of PP-g-MA-based masterbatches synthesized with water injection and high-shear rates.

In the last part of the thesis, we prepared PP/clay nanocomposites

by using the acquired knowledge reported in the preceding chapters. PP/clay nanocomposites were processed in one step through water-assisted extrusion using a PP-g-MA compatibilizer, native clay and a carboxylate salt. The *in situ* synthesis of carboxylate clay and PP-g-MA ionomer through sodium acetate addition and with the help of water injection was found to be an effective alternative to organoclays for the elaboration of PP/clay nanocomposites. The resulting composites show a much finer clay dispersion than without NaAc and water and present significantly enhanced thermal, rheological and mechanical properties, thus demonstrating the feasibility of the elaboration PP/clay composites from unmodified clay.

The optimized NBS-mediated PP-g-MA was compared to a corresponding PP-g-MA prepared without NBS for the elaboration of PP/clay nanocomposites using the aforementioned method, from both unmodified clay and organoclay. Whatever the clay and the compatibilizer employed, the combination of using water injection and sodium acetate addition always led to strong improvements of clay dispersion and properties enhancement. However, the NBS-mediated PP-g-MA, and even more its ionomer, were found to be much more effective as compatibilizers than the classic PP-g-MA and its ionomer. The highest clay delamination degree and the greatest enhancements of thermal and rheological properties were reached when combining the use of NBS-mediated PP-g-MA, sodium acetate, organoclay and water injection.

As a general conclusion, this work brought a significant contribution to the field of PP/clay nanocomposites. We have successfully revisited the traditional elaboration process, on the basis of a systematic and fundamental study of several key parameters. High level of clay delamination and significant properties improvements have been recorded for the novel PP/clay nanocomposites prepared through a one-step method, applicable to both unmodified clay and organoclay, and using trihydrate sodium acetate as additive and NBS-mediated PP-g-MA as compatibi-

lizer. A synergy effect of all the partners has been demonstrated.

Prospects

Highly functionalized elastomeric PP-g-MAs are immiscible with PP and therefore cannot be used as compatibilizers for PP/clay nanocomposites. However, such immiscible blends could be interesting for the preparation of thin films displaying nanostructures on their surface in the biomaterials field. Indeed, the biocompatibility is mainly governed by adhesion interfacial phenomena (proteins, cells, etc.) which depend, among other factors, on the surface topography. Moreover, the addition of clay to such immiscible blends could help controlling the size of the PP-g-MA droplets dispersed into the PP matrix. The covalent grafting of pro-adhesive molecules on the PP-g-MA domains could also be envisaged.

The use of *in situ* synthesized PP-g-MA ionomers is effective for increasing the clay dispersion and properties of PP-g-MA/clay and PP/clay nanocomposites. It should be interesting to examine the use of a PP-g-MA ionomer afore prepared as matrix or as compatibilizer in comparison with PP-g-MA ionomer *in situ* prepared. PP-g-MA ionomer/clay masterbatches could be also prepared in order to be diluted into neat PP. Indeed, better clay dispersion and higher properties enhancement were achieved when PP/clay nanocomposites are produced by dilution into neat PP of a PP-g-MA/clay concentrate rather than by direct melt blending of PP, PP-g-MA and clay.

The large scale production of the selected home-made PP-g-MA has to be optimized for obtaining similar PP-g-MA characteristics to the small-scale sample. In order to understand more deeply the elaboration mechanism of PP/clay nanocomposites, the position of the MA grafts onto the PP-g-MA chain must be investigated, for example by synthesizing PP-g-MA with MA enriched in ^{13}C and performing ^{13}C -

NMR analysis. This would help to discriminate between the end-chain or in-chain grafting. The position of the grafted moieties is important since, for example, PP/clay nanocomposites prepared using ammonium-terminated-PP have completely different behavior than those prepared using usual PP-g-MA as compatibilizers.

The addition of sodium acetate to PP-g-MA/unmodified clay or PP/PP-g-MA/unmodified clay blend is effective for increasing the unmodified clay dispersion and enhancing the composite properties. It should be interesting to prepare and investigate the properties of nanocomposites obtained by dilution into neat PP of PP-g-MA/sodium acetate/unmodified clay concentrates. The use of carboxylate clay with more polar matrix such as polyamide should also be examined. Since carboxylate clay remains relatively polar in comparison to usual alkylammonium clays, one can suppose that carboxylate clay would be easier to disperse into a polar matrix than into an apolar one.

The elaboration of PP/clay nanocomposites through water-assisted extrusion strongly improves the organoclay delamination and the nanocomposites properties. However, the effect of the amount of injected water should be examined. Other organoclays containing polar functions like carboxylic acid, ester or ether functions could be of interest.

Significant improvements in PP/clay nanocomposites properties have been obtained through a one-step preparation method from both unmodified clay and organoclay using optimized PP-g-MA, water injection and sodium acetate. However, the amount of sodium acetate remains to be adapted when using organoclay (only 4 wt.% was considered in the thesis). Moreover, in order to get PP/clay nanocomposites with stronger enhancement of mechanical properties, the adaptation of the present method to a masterbatch dilution process should be investigated.

Chapter 9

Curriculum vitæ

ROUSSEAUX Dimitri, Ph.D.

Education

- 2006–2010: **Ph.D. in Chemistry** (Polymer Sciences), Université catholique de Louvain (UCL), Belgium.
- 2006–2008: **DEA in Chemistry** (Polymer Sciences), Université catholique de Louvain (UCL), Belgium. (High honors).
- 2005–2006: **M.Sc. in Chemistry** (Organic Chemistry and Polymer Sciences), Université catholique de Louvain (UCL), Belgium. (High honors).
- 2003–2005: **M.Sc. in Chemical Engineering** (Polymers, paints and varnishes), Institut Meurice, Belgium. (High honors).
- 2000–2003: **B.Sc. in Chemistry** (Industrial Chemistry), Institut Paul-Lambin (IPL), Belgium. (High honors).

Experience

- 09/2006–09/2010: Researcher (Ph.D. thesis), Université catholique de Louvain (UCL), Belgium “Optimization of polypropylene/clay nanocomposites”.
- 09/2005–06/2006: Master thesis, Université catholique de Louvain (UCL), Belgium. “Grafting of maleic anhydride onto polyethylene”.
- 03/2005–08/2005: Erasmus/Engineer master thesis, University of Leeds, UK. “Nanoreplicated polymer for electronic circuit manufacturing”.
- 07/2004–07/2004: Engineer master internship, Mactac, Belgium. “Pressure sensitive adhesives”.
- 02/2003–06/2003: Bachelor internship, Université catholique de Louvain (UCL), Belgium. “Grafting of maleic anhydride onto polypropylene”.
- 09/2002–01/2003: Bachelor thesis, Université catholique de Louvain (UCL), Belgium. “Vanadium/Titanium catalysts for chloro-aromatic compound removal”.
- Other professional and social experiences: Supervisor of 7 bachelor theses/internships, member of the laboratory security and IT management teams during my Ph.D. thesis. Scout educator from 2000 to 2004. Student jobs during farm harvest from 1998 to 2003.

Skills

- Scientific skills:
Spectroscopy: FTIR, WAXS, SAXS, RMN
Thermal analysis: DSC, HP-DSC, TGA, DMA
Mechanical testing: tensile testing
Microscopy: SEM, TEM, OM
Rheology: capillary, plate-plate
Chromatography: GPC, HPLC, GC
Polymer processing single-/twin-screw extrusion, extrusion with water injection, injection moulding
Syntheses: Organic synthesis, Free-radical grafting synthesis on molten polymer.
- Languages: French (Native), English (Good), Dutch (Basic).
- Computer skills: Operating system: DOS, Windows, MacOS, Linux.
Software: Office, Latex, Origin, Igor, Endnote.
- Others: Security Industry First Aid Training (2010), scout educator certificate (2002), typewriting (1995), driving licence.

Interests

Scouting, volleyball, IT, home winemaking and brewing, cooking and gardening.

Publication list

Journal articles

- **Rousseaux D.; N., Baudouin A.-C., Devaux J., Godard P., Marchand-Brynaert J., Slavons M.,** *Polymer*. In Press. "Water-assisted extrusion of Polypropylene/Clay Nanocomposites: a comprehensive study".
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