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OPTIMIZATION OF MECHANICAL AND MOISTURE RESISTANCE OF
POLYETHYLENE WOOD PLASTIC COMPOSITES REINFORCED WITH
NANOCRYSTALLINE CELLULOSE

MONTREAL, NOVEMBER 4 TH, 2015



Foued BENSALÉM, 2015



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OPTIMISATION DES PROPRIÉTÉS MÉCANIQUES ET DE RÉSISTANCE À L'HUMIDITÉ DE COMPOSITES BOIS-PLASTIQUE À BASE DE POLYÉTHYLÈNE ET DE NANOCRISTAUX DE CELLULOSE

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RÉSUMÉ

L'ajout de nanoparticules dans les polymères thermoplastiques renforcés par des fibres de bois a été considéré comme l'un des moyens les plus efficaces pour améliorer les propriétés mécaniques et physiques des composites bois-plastiques. Dans ce contexte, l'objectif de ce travail est d'étudier l'effet d'incorporation des nanocristaux de cellulose (NCC) sur les propriétés mécaniques et l'absorption d'eau du composite bois-plastique à base de polyéthylène haute densité (HDPE) et de farine de bois.

La première phase a consisté d'étudier la faisabilité d'obtention du nanocomposite HDPE/NCC en utilisant un mélangeur. L'effet des paramètres de mise en forme, de concentrations de NCC (0%, 3% et 10% en poids) et d'agent de compatibilité sur les propriétés mécaniques, le taux d'absorption d'eau et de la dispersion des NCC a été analysé. Dans la deuxième phase, les conditions de préparation et de la formulation de nanocomposites HDPE/NCC obtenues à la première phase, sont utilisés pour la fabrication du composite hybride HDPE/NCC/farine de bois. Des tests de propriétés mécaniques (flexion et traction) et d'absorption d'eau ont été réalisés pour évaluer la performance du composite.

Les résultats ont montré qu'une augmentation de la teneur en NCC jusqu'à 10% conduit à une amélioration significative des propriétés en flexion et en traction de nanocomposites HDPE/NCC. Toutefois, l'analyse de la dispersion des NCC avec le microscope électronique à balayage (MEB) a montré la présence de grosses agglomérations quelques soit la concentration d'agent de compatibilité. Le remplacement partiel de farine de bois avec 10% de NCC n'a pas montré aucune amélioration de la résistance en flexion et en traction du composite hybride bois-plastique. Cela est peut-être dû aux problèmes de compatibilité entre les NCC et la matrice HDPE, et aussi à la mauvaise dispersion des NCC en présence d'une haute concentration. En revanche, une légère baisse du taux absorption d'eau a été détectée dans le cas du composite hybride qui peut être causé par la différence de caractère hydrophile entre la farine de bois et les NCC.

Plus de tests avec la modification de surface et du dosage liquide des NCC devrait être fait pour améliorer la performance des nanocomposites hybrides HDPE/bois/NCC. En outre, l'effet de la concentration NCC peut être étudié pour identifier le seuil de percolation dans le composite.

Mots clés: Composite bois plastique, nanocristaux de cellulose, hybride, dispersion, HDPE.

OPTIMIZATION OF MECHANICAL AND MOISTURE RESISTANCE OF POLYETHYLENE WOOD PLASTIC COMPOSITES REINFORCED WITH NANOCRYSTALLINE CELLULOSE

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ABSTRACT

The addition of nanoparticles in polymers reinforced with wood fiber has been considered as one of the most effective way to improve the mechanical and physical properties of wood-plastic composites. In this framework, the objective of this study was to investigate the effect of incorporation of nanocrystalline cellulose (NCC) on the mechanical properties and water absorption of wood-plastic composite made from high density polyethylene (HDPE) and wood flour.

The first phase of this project involved the reinforcement of HDPE matrix with NCC using internal mixer. The effect of processing conditions, NCC content (0%, 3% and 10% wt.) and compatibilizing agent on the mechanical properties, water absorption rate and dispersion of NCC was analyzed. In the second phase, the best compounding conditions of HDPE/NCC nanocomposite, obtained from the first step, was used for the preparation of hybrid wood plastic composite. Mechanical properties (flexural and tensile) and water uptake were carried out to evaluate the performance of the composite.

Mechanical results showed that the increase of NCC content until 10wt. % lead to the increase of flexural and tensile properties of HDPE/NCC nanocomposite. However, the SEM analysis of NCC dispersion showed the presence of big agglomerations. For Hybrid HDPE/NCC/WF composite, a partial replacement of wood flour with 10% NCC did not show any improvement in the flexural and tensile properties. This is due to the poor dispersion of NCC. In contrast a slight decrease of water absorption was detected in hybrid composite which can be caused by differences of hydrophilicity between wood flour and NCC. In further work, more tests with surface modification and liquid feeding of NCC should be done for successful development of hybrid wood nanocomposite. Also, the effect of different NCC concentration can be realized to identify the percolation threshold of composite reinforcement.

Key words: Wood plastic composite, nanocrystalline cellulose, hybrid, dispersion, HDPE.

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LIST OF ABBREVIATIONS

ASTM	American society for testing and materials
CAB	Cellulose acetate butyrate
Cloisite Na ⁺	Natural montmorillonite
Cloisite 10A	Montmorillonite modified with quaternary ammonium salt
Cloisite 15A	Montmorillonite modified with quaternary ammonium salt
Cloisite 20A	Montmorillonite modified with quaternary ammonium salt
Cloisite 25A	Montmorillonite modified with quaternary ammonium salt
Cloisite 30B	Montmorillonite modified with quaternary ammonium salt
DMAc	N,N- Dimethylacetamide
DMF	N, N-dimethylformamide
GTA	Glycerol triacetate
HDPE	High density polyethylene
LDPE	Low-density polyethylene
LiCl	Lithium chloride
LMFI	Low melt flow index
MAPP	Maleated polypropylene
MCC	Microcrystalline cellulose
MMFI	Medium melt flow index
Nano-SiO ₂	Silica dioxide nanoparticles
NCC	Nanocrystalline cellulose
NFC	Cellulose nanofibers
PEG	Polyethylene glycol

PHBV	Poly(3-hydroxybutyrate-co-3-hydroxyvalerate)
PLA	Polylactic acid
PP	Polypropylene
PVA	Polyvinyl acetate
SEM	Scanning electron microscopy
TEC	Triethyl citrate
TEM	Transmission electron microscopy
TEMPO	(2,2,6,6-tetramethylpiperidin-1-yl)oxyl
TiO ₂	Titanium dioxide
WF	Wood flour
WPC	Wood-plastic composites

INTRODUCTION

✓ Background and problematic of research

During the last decade, wood-plastic composites (WPC) have emerged as an important family of engineering materials. Compounding polymers with wood flour and wood fibers is a common practice and has been done in industry and studied by academics, to reduce cost and attain desired properties. Wood fibers can provide weight savings, higher specific tensile strength and modulus, good processing and low impact against the environment. These properties allow wood fibers to replace the conventional inorganic reinforcements as glass and carbon fibers. However, despite these attractive properties, the potential for use WPC in many industries including construction, automotive and decking has been limited for their high moisture absorption, high brittleness, low impact resistance, lower bending stiffness and mainly high density compared to the neat plastic. Poor mechanical properties are mainly due to the poor interfacial interactions between hydrophilic fibers and hydrophobic polymer.

Therefore, most studies in the area of WPC focus on improving the physical and mechanical properties of the composites by the improvement of interfacial adhesion between wood fibers and hydrophobic thermoplastics.

To supplement this deficiency in compatibility, several approaches have been used in the literature including the introduction of coupling agents or various other chemical and physical surface modifications.

Another promising approach to improve the mechanical properties such as interfacial strength is producing hybrid composites with the combination of wood fibers and several nano-sized particles like carbon nanotube, nanoclay, and cellulose nanocrystals. Indeed, nanoparticle exhibit high aspect ratio and high surface area, which can be beneficial to improve the interfacial interaction between fiber and polymer by increasing the contact surface with polymer and present into minor zone where the fibers cannot reach. Moreover, the abundance of functional groups at the surface of nanoparticles can offer new possibilities to the development of multifunctional materials (antibacterial and electrical conductivity) with the grafting of new groups. In the literature, many studies have found that a synergistic effect can occur between the wood fibers and nanoparticles like nanoclay (Zhao, Wang et al.

2006, Faruk and Matuana 2008, Hemmasi, Khademi-Eslam et al. 2010, Deka and Maji 2013), carbon nanotube (Fu, Song et al. 2010, Kordkheili, Farsi et al. 2013, Farsi and Sani 2014, Kushwaha, Pandey et al. 2014, Nourbakhsh, Ashori et al. 2015), nano-SiO₂(Deka and Maji 2013, Deka, Baishya et al. 2014) and TiO₂(Deka and Maji 2011). However, to exploit this real positive effect of nanoparticles, an improvement in their dispersion in polymer matrix is required.

In this regards, cellulose nanocrystals (NCC), obtained by hydrolysis of native cellulose acid, present a high potential source of innovation for the reinforcement of composite materials in various engineering applications. These nanoparticles are characterized by a high crystallinity and nano rods section with a very high specific surface area (a length of 5 to 10 nanometers and a width of 100 to 500 nanometers). Although much research has been done in the field of NCC based nanocomposite, only a few papers have reported the effect of combination of cellulose nanocrystal and wood fibers to improve interfacial adhesion and mechanical properties of hybrid nanocomposite (Ashori and Nourbakhsh 2010, Nourbakhsh, Ashori et al. 2010).

High density polyethylene (HDPE) has long been used in a variety of applications due to its versatile properties such as good mechanical properties, good chemical resistance and good processability when using conventional manufacturing process. However, to expand its field of application and increasing its mechanical properties, a variety of methods such as filling or blending were adopted. For this purpose, during the last decade, glass fibers and wood flour have been the two common materials mainly used for reinforcement of HDPE. However, the problem of adhesion between the hydrophilic fibers and hydrophobic HDPE matrix and the difficulty of filler dispersion in the polymer are the main challenges to be solved. In order to overcome interfacial incompatibility issues in wood flour reinforced HDPE the use of a NCC and coupling agent such as maleic anhydride can be one of the best solution of this problem.

✓ **Research hypothesis**

Improving the mechanical and physical properties of composites depends not only on the characteristics of each component but also the interactions at the interface between the matrix and the reinforcements. For this reason, achieving a good adhesion between the polymer matrix and the fibers as well as a good dispersion of fibers within the polymer matrix is

critical to obtain a good composite. Increasing the contact surface area by adding a small amount of nano sized particles in WPC could be a solution for that purpose. Moreover, the abundance of functional groups at the surface of nanoparticles can offer new possibilities to the development of multifunctional materials (antibacterial and electrical conductivity) through the grafting of different chemical groups. Therefore, in this work, the possibility of adding NCC as improve the interfacial adhesion between fiber and polymer by increasing the contact surface between the polymer and the wood fibers was investigated.

The present work was based on the following hypothesis:

Adding nanoparticles, in particular NCC to WPC could allow:

- An increase of the compatibility between polymer matrix and wood fibers
- An increase of the interaction between polymer and fibers due to the large surface area of NCC
- An increase of the interaction between maleic anhydride which can be grafted to the polymer matrix and the hydroxyl groups at the surface of NCC
- A filling the cavities between the fibers and the polymer which is beneficial for water uptake resistance.

✓ **Objective of study**

As mentioned earlier, incorporation of nanoparticles in the wood plastic composite is among the proposed approaches for improving mechanical properties and water absorption. In particular, nanocrystalline cellulose (NCC) has presented a growing interest as promising reinforcement in polymer systems because of its interesting mechanical properties and the abundant and renewable sources of cellulose.

For this purpose, the main objective of this research was to investigate the effect of adding nanocrystalline cellulose (NCC) on the mechanical properties and water absorption of HDPE/wood flour composite. This information can help to find out the reinforcement potential of NCC in HDPE composites.

Therefore, the specific objectives of the present study were:

- To establish an effective experimental methodology for incorporation of NCC in HDPE/wood flour composite;

- To compare the effect of two maleic anhydride types with various concentration on mechanical properties and moisture resistance of HDPE/NCC composite;
- To study the effect of adding NCC on mechanical properties and water absorption of HDPE/wood flour composite.

In this framework, different approaches were examined to identify the best compounding conditions and the appropriate nanoparticles concentration to be added into molten polymer. For a successful obtention of HDPE/NCC nanocomposites, two coupling agents developed by Dupont were tested to improve the dispersion of NCC in HDPE. Tensile and flexural properties, water absorption and morphology of the nanocomposites HDPE/NCC and hybrid composite HDPE/wood flour/NCC were examined to identify the best compounding conditions for obtaining the composite.

✓ **Structure of the dissertation**

The dissertation will be presented in five chapters:

Introduction deals with the presentation of the background and problematic of the proposed research and the different targeted objectives.

Chapter 1 is devoted to providing an overview of wood plastic composite, their advantages, principal drawbacks and the conventional methods adopted for their improvement. Then, the research progress on HDPE nanocomposites, NCC reinforced composites and the hybridization effect on mechanical properties and water absorption of wood plastic composite by incorporation of nanoparticles was presented. The various surfaces modification methods and processing techniques for improving nanoparticles dispersion are detailed in this part

Chapter 2 presents the materials and methods used in this project to prepare the different composites formulations and characterization techniques adapted to evaluate the morphology, mechanical and physical properties of composites.

Chapter 3 consists of a discussion and analysis of principal results obtained in this work.

Chapter 4 is dedicated to presenting the different conclusions drawn from our project and the main recommendations for further work.

CHAPTER 1

LITERATURE REVIEW

This chapter presents a review of literature on the effect of nanoparticles (NCC) on the mechanical properties and water uptake of NCC nanocomposites and an evaluation of their reinforcing potential in nanocomposite manufacturing. In addition, a review of the synergistic effect by combining wood fibers and nanoparticles to improve the interfacial interactions between fibers and matrix was discussed.

1.1 Wood plastic composite (WPC)

1.1.1 Interest of WPC

Wood plastic composite (WPC) is a composite material made by the combination of wood, in various forms (flour, fibers, dice), and plastic polymer such as polyethylene, polypropylene and PVC. These materials exhibit the appearance and rigidity of wood and surface smooth and weathering resistance of plastic. Using wood fibers in polymer composite has become a new common practice to replace traditional composite made of glass fibers. In the last few decades, WPC are starting to get a considerable popularity in various applications fields. The most important application for WPC are building (decking, floor, walls, windows and fencing) (Moffit 2012, Brunette 2013, Industry 2013), automotive interior parts and many other applications such as furniture, sports and some electronic devices (Brief 2011, Carus 2011, Brunette 2013). Figure 1.1 shows the different application fields of WPC produced in Europe. Decking is the main application of WPC with 67% of total production. Between 2014 and 2019, the wood plastic composite is expected to grow from \$2579.90 million to \$4,601.7million (Kulkarni and Mahanwar 2013, Tiwari 2015).

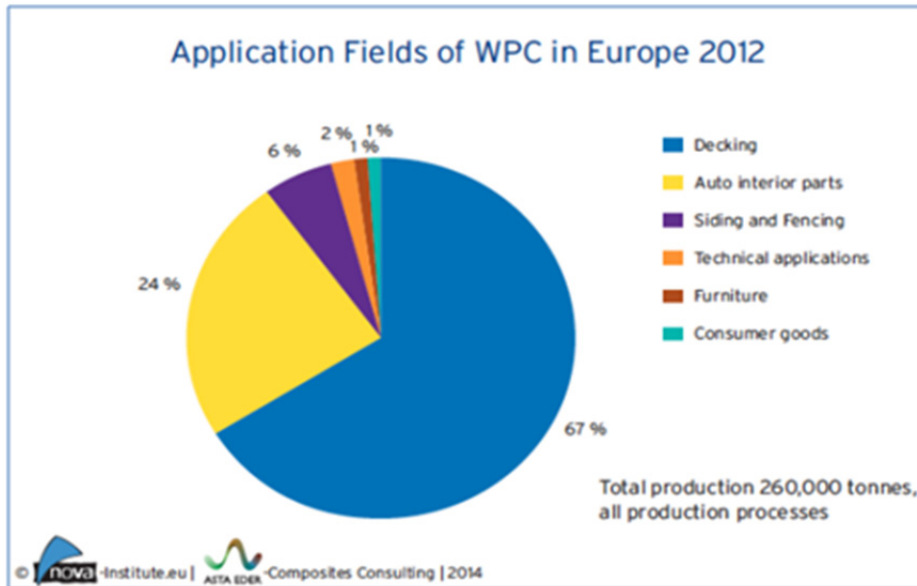


Figure 1.1 Application fields of WPC in Europe in 2012
(Kulkarni and Mahanwar 2013, Tiwari 2015)

1.1.2 Failure of WPC

During the last decades, several studies on wood plastic composites (WPC) have been reported in the literature (Woodhams, Thomas et al. 1984, Jayaraman and Bhattacharyya 2004, Jiang and Kamdem 2004, Ashori 2008, Jördens, Wietzke et al. 2010, Kumar, Tyagi et al. 2011, La Mantia and Morreale 2011). Polyolefins such as high-density polyethylene (HDPE), low-density polyethylene (LDPE), and polypropylene have long been the most popular polymers used as a matrix of WPC. Adding wood fibers as inexpensive fillers provides, in general case, a great ability to improve mechanical properties of polyolefins (Julson, Subbarao et al. 2004, SLAMA 2008, Petinakis, Yu et al. 2009, Altun, Doğan et al. 2013). However, despite the recent success of WPC, their applications are still limited in industrial practice due to their hydrophilic nature, thickness swelling and defective interfacial stress transfer between fibres and matrix (Sretenovic, Müller et al. 2006). Tensile modulus and flexural modulus, generally, increase gradually when fibres concentration increases (SLAMA 2008, Petinakis, Yu et al. 2009, Altun, Doğan et al. 2013). Nevertheless, at very high filler loading, the mechanical properties of composite start to decline due to poor dispersion and

fibres damage during processing by the increase of shear stress and fibre-fibre friction (Beg 2007). Soucy et al. (SOUCY 2007) and Li et al (Li 2012), reported that a maximum of 60 w% of wood fibres should be respected to avoid a decrease of the mechanical properties of WPC. In contrast, tensile strength (Englund 1999, Balasuriya, Ye et al. 2001, Karmarkar, Chauhan et al. 2007, Adhikary, Pang et al. 2008) and flexural strength (Balasuriya, Ye et al. 2001, Adhikary, Pang et al. 2008) have, generally, remained stable or sustained a slight decrease due to the poor dispersion. The effect of wood fibre on tensile and flexural properties of HDPE and PS composites obtained by Michael P. Wolcott et al. (Englund 1999) and P.W Balasuriya et al. (Balasuriya, Ye et al. 2001) is shown in Figure 1.2 and Figure 1.3.

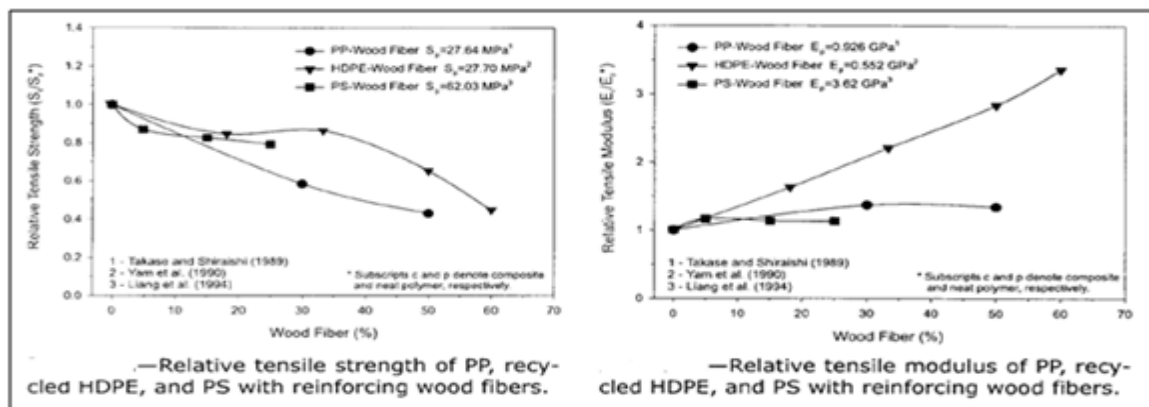


Figure 1.2 Effect of wood fiber content on tensile strength and modulus of WPC (Englund 1999)

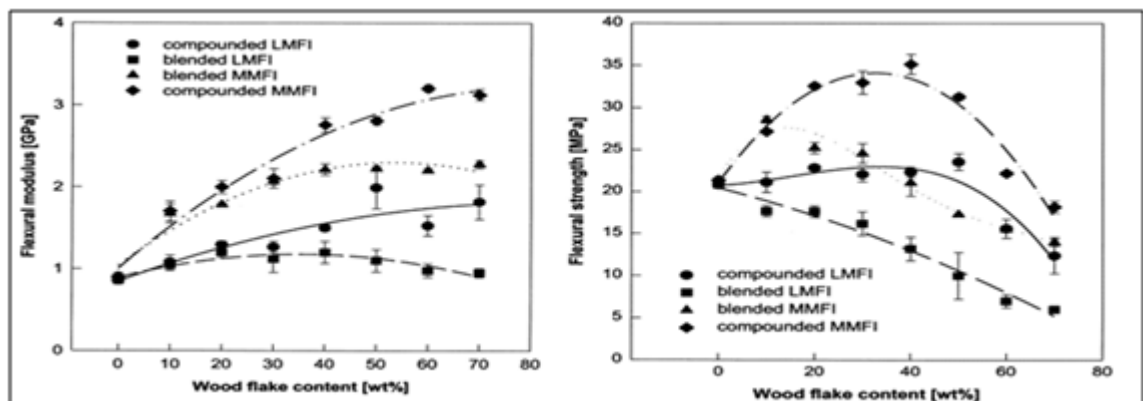


Figure 1.3 Effect of wood fiber content on flexural strength and modulus of WPC composites based on different HDPE and processing techniques (Balasuriya, Ye et al. 2001)

To overcome the decrease of mechanical propriety of WPC, good stress transfer from the matrix to the reinforced fibers must be achieved. Improving compatibility and dispersion of wood fiber is the main key for increasing the mechanical properties of composite. Low ductility, low impact strength and water absorption resistance are also a challenge for the implementation of WPC in many application fields. As in case of tensile strength, impact resistance of wood plastic composite decreases with increasing fillers concentration (Balasuriya, Ye et al. 2001, Karmarkar, Chauhan et al. 2007, Yang, Wolcott et al. 2007). Balasuriya et al. (Balasuriya, Ye et al. 2001) investigated the mechanical properties of HDPE reinforced wood flake composite prepared by twin extruder. They reported that impact strength of WPC, prepared using different processing conditions, decrease with an increase in wood flake content (shown in Figure 1.4). This trend was explained by the poor interfacial adhesion between wood flake and HDPE.

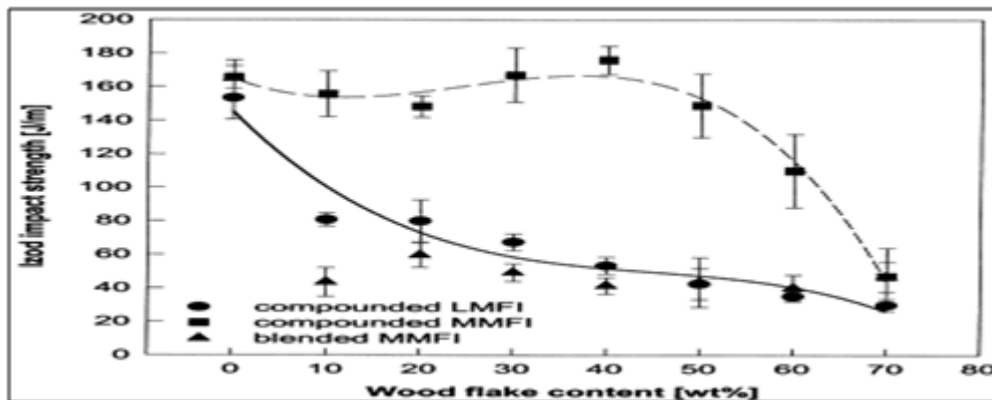


Figure 1.4 Effect of wood fiber content on Izod impact strength of WPC composites based on different HDPE(LMFI: low melt flow index and MMFI : medium melt flow index) and processing techniques (Balasuriya, Ye et al. 2001)

In addition to the failure of mechanical properties of WPC, higher water absorption and thickness swell can also be found as a negative effect of using wood fibers in polymer composites(Tajvidi and Ebrahimi 2003, Adhikary, Pang et al. 2008, Soury, Behravesht et al. 2013). The high polarity of wood fibers results in increase of water absorption and low dimension stability (swelling) of WPC. Therefore, poor compatibility and interfacial adhesion between wood and polymer results in decrease of mechanical and physical

properties of wood plastic composite. One way to supplement this deficiency of WPC consists of adding coupling agents or various other chemical and physical surface modifications.

1.1.3 Traditional strategies for composite improvement

A strong fiber-matrix interface interaction is a challenge to improve adhesion and provide high mechanical properties of composites (Mohanty, Misra et al. 2001). Wood fibers are hydrophilic in nature which reduce their compatibility with hydrophobic polymer and increase water absorption of composite. To overcome this drawback of wood fibers and strengthening interfacial adhesion, the surface of the fibers can be modified by physical or chemical means (Mohanty, Misra et al. 2001, Kalia, Kaith et al. 2009, Mukhopadhyay and Fanguiero 2009). Several modification methods have been proposed in the literature such as alkaline treatment (Ichazo, Albano et al. 2001, Altun, Doğan et al. 2013), isocyanate treatment (Karmarkar, Chauhan et al. 2007, Petinakis, Yu et al. 2009), corona (Ragoubi, Bienaimé et al. 2010, Ragoubi, George et al. 2012) and plasma (Acda, Devera et al. 2012, Gibeop, Lee et al. 2013) discharge and chemical coupling with silanes (Pickering, Abdalla et al. 2003, Abdelmouleh, Boufi et al. 2007, Yanling Wang 2011) or maleic anhydride coupling agent (Kazayawoko, Balatinecz et al. 1999, Lai, Yeh et al. 2003, Sombatsompop, Yotinwattanakumtorn et al. 2005, Kim, Lee et al. 2007, Majeed, Hassan et al. 2014). The main objective of all these modifications is to increase hydrophobicity by substitution of hydroxyl groups at the surface of wood fibers and make better interfacial adhesion with polymer matrix. Using polyolefin to which maleic anhydride is grafted is the most popular method today to obtain WPC due to its relatively cheap price, and success in showing good compatibility to the wood fibers. However, despite the considerable success of those surface modification techniques, they suffer from several limitations such as for example: a risk of structure modification or degradation of fibers during chemical treatment with alkaline and a non-environmentally friendly and uneconomical process. On the other hand, the improvement achieved with using coupling agent is limited by the concentration of maleic anhydride and its tendency to migrate at the interface during processing. Some research examined the effect of adding coupling agent to the mechanical properties of wood

composite. They reported that compatibilized wood fibers presented much better mechanical strength and stiffness enhancement than incompatibilized fibers (Karmarkar, Chauhan et al. 2007, Kord 2011, Ou Rongxiana 2011). However, the properties of composite were deteriorated with excess of coupling agent due to the increase of polymer/coupling agent immiscibility and its entanglements and slippages (N/A, Kato, Usuki et al. 1997).

1.2 Hybrid wood nanocomposite

Recently, a new way to improve mechanical properties of WPC can be represented by the addition of small amounts of nano-sized fillers such as nanoclay (Zhao, Wang et al. 2006, Faruk and Matuana 2008, Hemmasi, Khademi-Eslam et al. 2010, Deka and Maji 2013), carbon nanotubes (Fu, Song et al. 2010, Kordkheili, Farsi et al. 2013, Farsi and Sani 2014, Kushwaha, Pandey et al. 2014, Nourbakhsh, Ashori et al. 2015) and nanocrystalline cellulose (Nourbakhsh, Ashori et al. 2010, Yang, Peng et al. 2015). This type of composite is a so called hybrid nanocomposite. An increased interest of scientists and researchers has been granted for the investigation and understanding the mechanical and physical behavior of hybrid nanocomposite. Figure 1.5 gives an overview of articles published in the literature on the development of these materials.

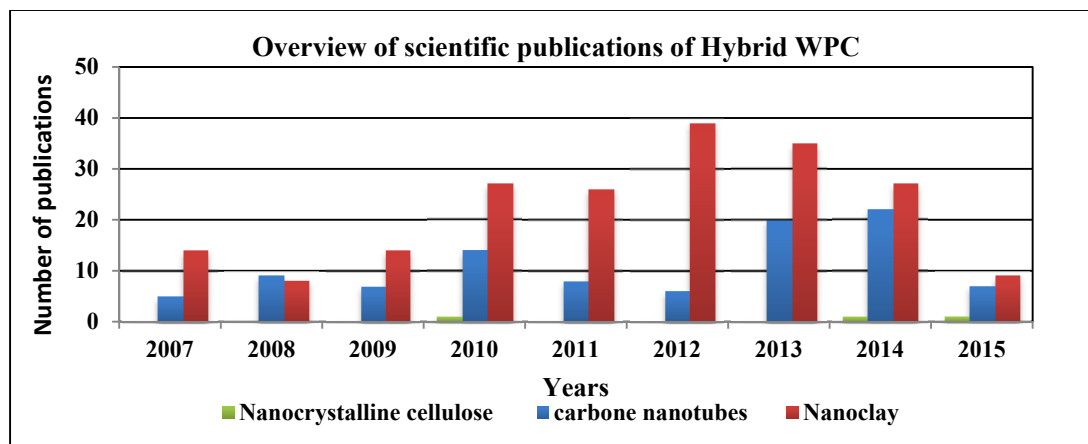


Figure 1.5 Trends in the number of articles published on hybridization of wood plastic composite with nanofillers between 2007 and 2015. Key words used are "wood plastic"; and "nanocrystalline cellulose" or "nanoclay" or "carbon nanotubes" (source Compendex & INSPEC ETS library accessed 07/08/2015)

When added to WPC, the inclusion of nanofillers may result in a new possibility to improve adhesion and result in better performances that cannot be obtained with traditional surface modifications. In fact, due to their small size, nanofillers have extremely high specific surface area which makes a larger interface and a strong interaction between the fillers and the matrix. Using a combination of two kinds of fillers not only can improve mechanical properties and wood fiber dispersion, but also add a new functionality to WPC such as electrical conductivity (Faruk and Matuana 2008), flame retardancy (Guo, Park et al. 2007, Lee, Kuboki et al. 2010), water resistance (Gu, Kokta et al. 2010, Yeh and Gupta 2010) and barrier property (Turku and Kärki 2013). Nevertheless, good dispersion and agglomeration phenomena of nanoparticles still a critical challenge to have a synergistic effect between wood fibers and nanofillers. In fact, successful use of nanofillers in wood hybrid composite required a decrease of particle-particle interactions by increasing the interfacial adhesion with polymer matrix.

Therefore, an overview of the progress in this research area will be presented in the next part to investigate the effect of adding nanocrystalline cellulose in HDPE wood plastic composite. The dispersion techniques approach will be also discussed.

1.2.1 Nanocomposites based NCC

1.2.1.1 Polymer nanocomposites

Nanocomposites are composites in which one or more of these components have a dimension in the nanometre range (1-100 nm). In the last few decades, these materials have attracted much academic and industrial attention in various application areas such as automotive, aerospace, electronics, pharmaceutical and biotechnology.

Growth of industrial interest in nanocomposites is reflected by the increasing of global consumption of these products in recent years. Between the years 2014 and 2019, the market was expected to increase from nearly 225,060 metric tons in 2014 to nearly 584,984 metric tons in 2019 (Reddy 2010, BCC 2014) as seen in Figure 1.6.

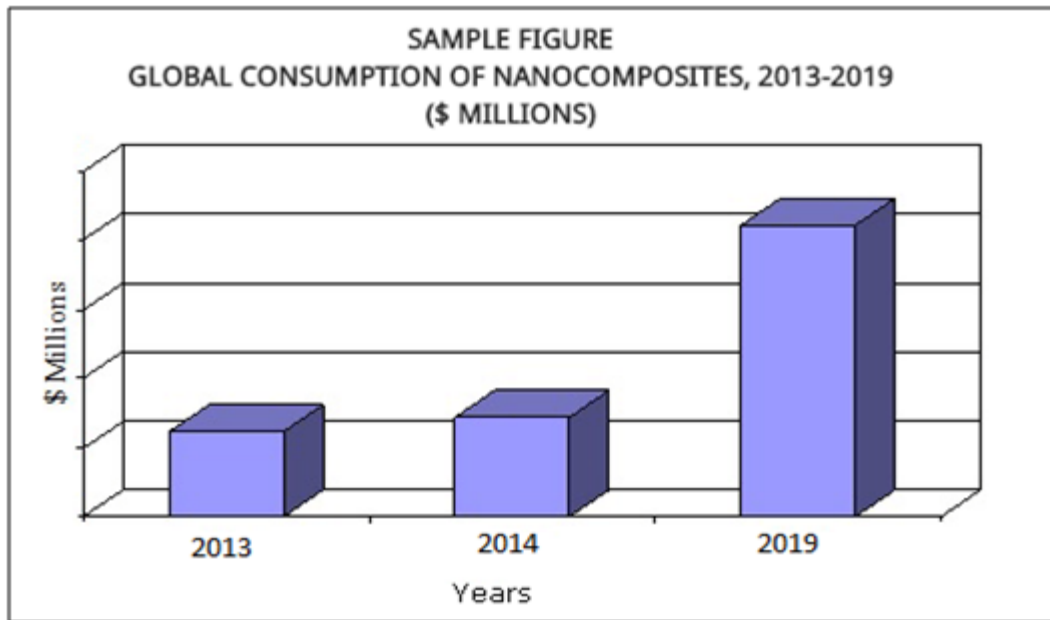


Figure 1.6 Global consumption of nanocomposites from 2013-2019 (Reddy 2010, BCC 2014)

Addition of nanoparticles as fillers in the polymer matrix appears as a high-potential for the improvement of mechanical properties as strength, rigidity and flexibility and physical properties as barrier properties, thermal resistance and electrical conductivity of polymer composite. Compared to conventional micro-fillers, nanoparticles have a very high surface area to volume ratio (shown in Figure 1.7) and high surface energy which allows them to have more chemical interactions with polymer surface and therefore enhance the interfacial adhesion of materials. As shown in Figure 1.7, the decrease of particle size (cube) from 27 mm in length to 5 nm results in a significant increase in the number of small cubes in the same volume, which going from 1 to 1.6×10^{23} cubes and an increase of surface area that reaches 2 Km^2 (Hanemann and Szabó 2010, Reddy 2010). The high surface area of nanoparticles makes it possible to use only a small amount of nanofillers to have the same mechanical results of conventional composite (using high fibres content).

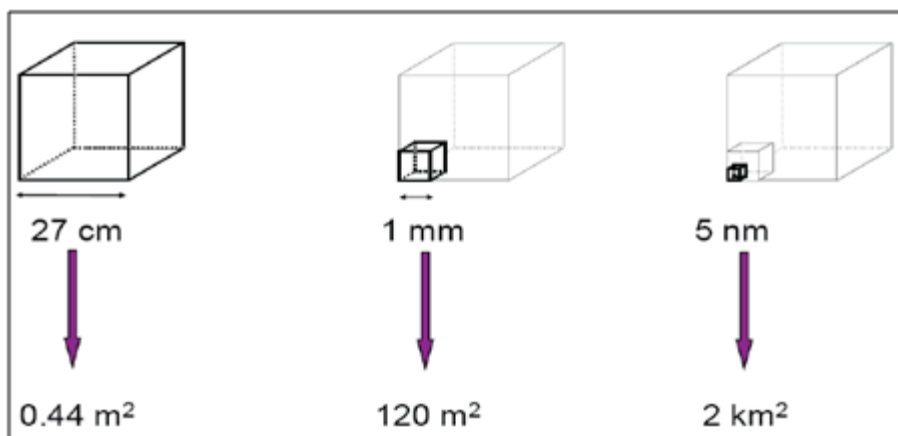


Figure 1.7 Increase of the specific surface area depending on the particles size (adopted from (Reddy 2010) and (Hanemann and Szabó 2010))

This abundance of functional groups on the surface of nanoparticles can, also, make easier their compatibilization with different coupling agents. However, despite these attractive advantages, increasing surface area leads to an increase of particle- particle interactions and their agglomeration which hence to a decrease of the mechanicals properties. Suttiponparnit et al.(Suttiponparnit, Jiang et al. 2011) and Vahid Khoshkava (Khoshkava 2013) were reported that an increase of surface area of nanoparticle cannot give a good results except if a good dispersion was reached. For this reason, good dispersion and distribution of nanoparticles must be achieved to exploit all the real strength of nanocomposites which usually not easy to get.

1.2.1.2 Nanocrystalline cellulose (NCC)

❖ Origin

Nanocrystalline cellulose (NCC) is a crystalline structural polysaccharide obtained from acid hydrolysis of native cellulose as described by Revol et al (Revol, Bradford et al. 1992). Compared to natural fibers and wood fibers, NCC presents several key features as a reinforcing agent in nanocomposites materials: such as nano-scaled dimensions with a very high aspect ratio and surface area (100 to 500 nanometers in length and 5 to 10 nanometers in

width) (Gilberto, Julien et al. 2010), high strength and modulus (Goetz, Mathew et al. 2009, Siqueira, Bras et al. 2010) and a good optical properties (inc , BIDEAU 2012). Those numerous advantages of NCC were combined with the abundance of biomass resources and their renewability to make of them as new bio-based fillers on polymer nanocomposites.

The isolation of NCC from cellulose resource materials can be done using a mechanical separation process of nanofibrils (amorphous regions and crystalline regions) followed by a chemical treatment, generally hydrolysis, to remove the amorphous regions and obtain the pure crystalline structure of cellulose (Brinchi, Cotana et al. 2013) (shown in Figure 1.8). This high crystallinity (between 54 and 88% (Moon, Martini et al. 2011, Brinchi, Cotana et al. 2013)) was the main cause of mechanical strength and chemical resistance of NCC.

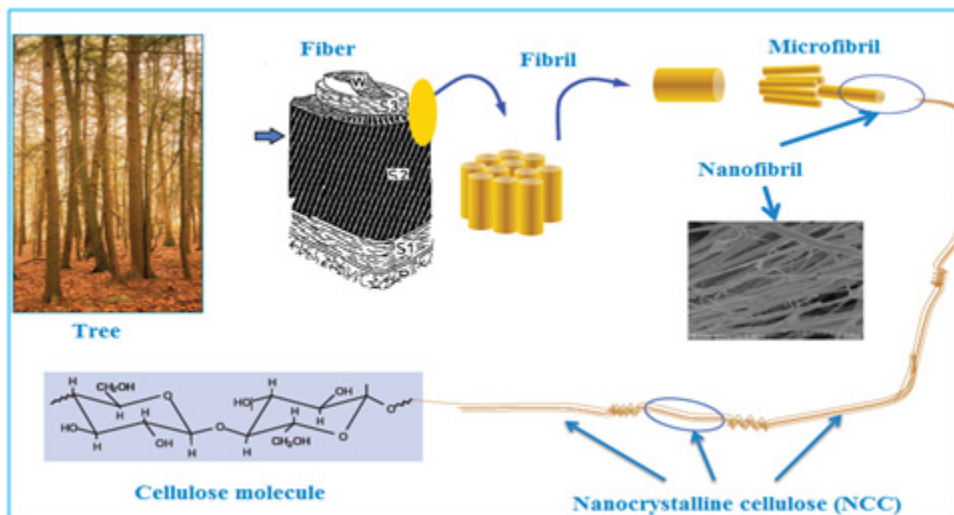


Figure 1.8 Schematic representation of the hierarchy structure of cellulose (W. N. HAWORTH 1930)

❖ Chemical structure and morphology

Microscopic analysis of NCC morphology shows that NCC is a rigid nanowhisker crystal with a dimension of 100 to 500 nanometers in length and 5 to 10 nanometers in width. The shape and size of nanoparticles are depending on plant source and acid hydrolysis conditions (shown in Figure 1.9).

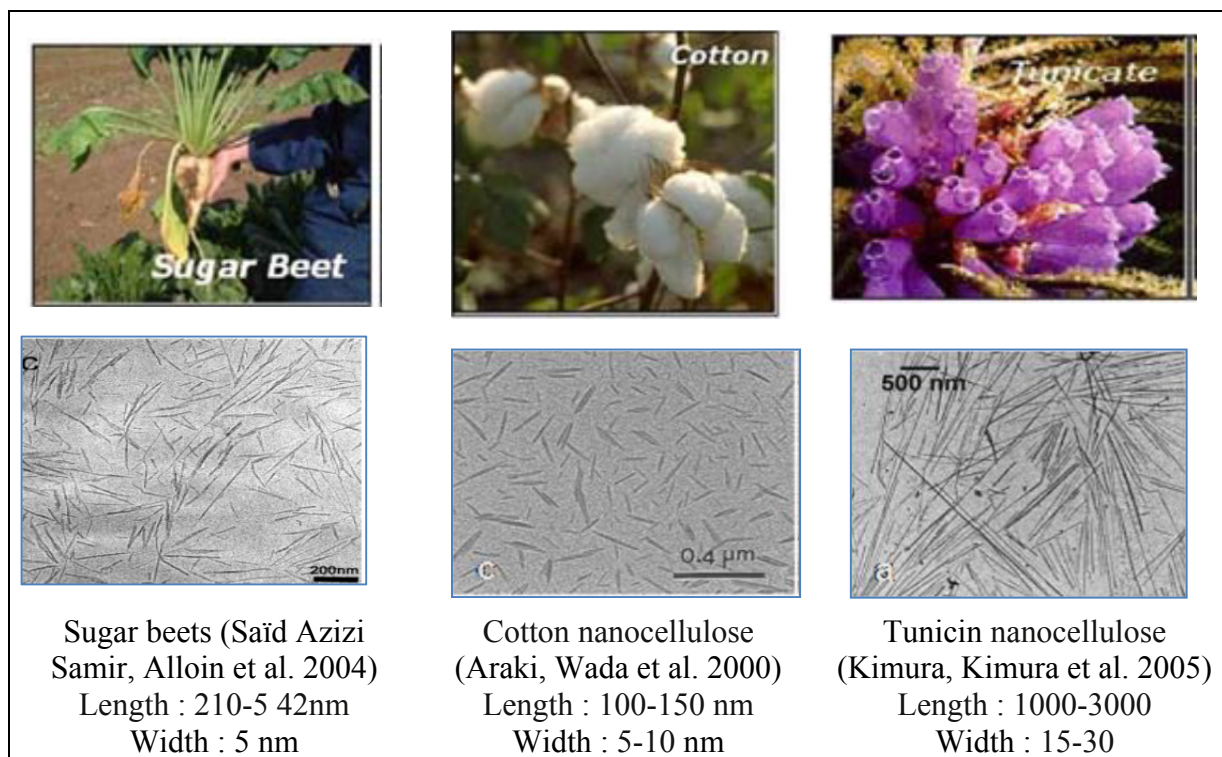


Figure 1.9 Several cellulose particle types according to their origin

Regardless of their source or size, at the macromolecular scale, the chemical structure of NCC is composed of two anhydroglucose units forming cellobiose [39] (see Figure 1.10). Each entity of cellobiose has 3 hydroxyl groups of which 2 secondary alcohol functions were in positions C2 and C3 and one primary alcohol function in position C6. These hydroxyl groups are responsible for the formation of intramolecular and intermolecular hydrogen bonds in cellulose. The abundance of these hydrogen bonds is the responsible for the linear structure of cellulose, mechanical strength, chemical resistance and thermal resistance (Mazza 2009) .

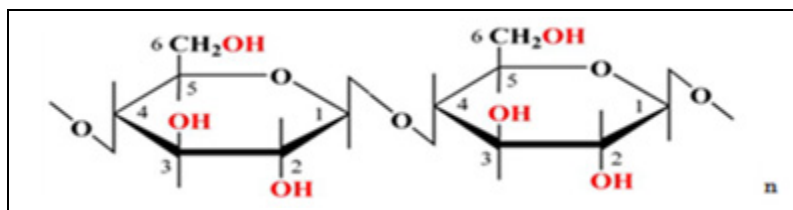


Figure 1.10 Chemical structure of cellulose

1.2.1.3 Challenge of nanocomposite dispersion

A better dispersion of nanoparticles is a key challenge to achieve desired performances of polymer nanocomposites. Therefore, it has been proven in many researches that mechanical and physical properties of nanocomposites were mainly governed by the degree of nanoparticles dispersion in polymer matrices (Pukánszky and Fekete 1999).

To explain the interfacial adhesion mechanism between the fibres and polymer matrix, several theoretical approaches have been proposed in the literature (ROCHE, #160 et al. 1991, Ragoubi 2010) such as mechanical theory (McBain and Hopkins 1924) (based on surface roughness), thermodynamic theory (Khoshkava and Kamal 2013) (based on wetting parameter and surface energy), diffusion theory (Voyutskii and Voiutskii 1963) (based on the affinity between fillers and polymer) and chemical theory (Peng, Dhar et al. 2011) (based on the formation of chemical bonding with or without using coupling agent). In our study, we have limited in chemical approach to understanding the effect of dispersion in interfacial adhesion between fillers and matrix.

In this regard, the interfacial interactions between filler and polymer leads to a good stress transfer between the matrix and nanofillers and the formation of strongly interphase with properties different from those of both components (Pukánszky and Fekete 1999, Fu, Feng et al. 2008). These interactions are controlled by the chemical bonding between the polymer and the fillers. However, in most of the cases the polymers are incompatible with nanofillers and a uniform dispersion is difficult to achieve. This lack of adhesion can cause the formation of strongly bonded nanoparticles agglomerations during the processing compounding of nanocomposites, which may further result in a failure of physical and mechanical properties of the final composite. In addition, the high surface area and the low particle size of nanofillers increases the tendency of nanoparticles agglomeration by increasing the particle-particle interactions. When these interactions are greater, they can result in a weak interphase and, consequentially, deteriorate the mechanical properties of nanocomposites (Móczó and Pukánszky 2008).

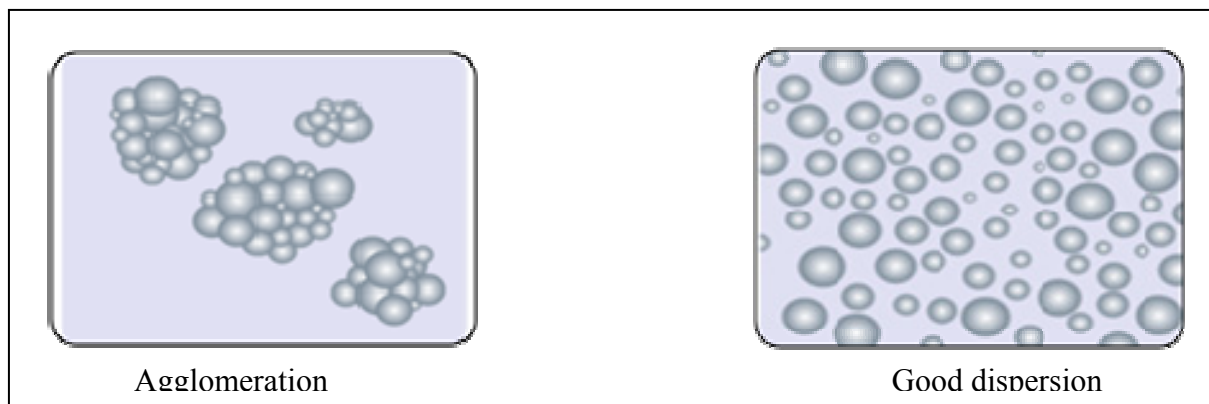


Figure 1.11 Dispersion of nanofibers in the plastic matrix

Therefore, to avoid this problem and reach a good dispersion, some preparation methods of nanoparticles were proposed. One of those attempts was focused on the surface modification by chemical substitution of new functional groups on the surface of nanoparticles to improve their compatibility with polymer matrix and reduce the particle-particle interactions.

1.2.1.4 Dispersion of NCC in plastic matrix

Because of the abundance of hydroxyl groups ($-OH$ groups) on the surface of nanocrystalline cellulose, their dispersion in a polar polymers has become a critical challenge. In fact, each OH groups on the surface has a tendency to form a weak hydrogen bonding with its adjacent (Deng, Zhang et al. 2012). As it was explained in the previous section, the formation of these intermolecular chains results in a poor dispersion and agglomeration of NCC inside the polymeric matrix. This lack of dispersion conditions, limits the mechanical properties of the prepared nanocomposite. To overcome these problems and improve the dispersibility of NCC, different surface modifications of NCC have been conducted to introduce new functional groups. These chemical groups may allow reducing the particle-particle interactions and, consequently, promote the NCC-polymer interactions. Such modifications can be obtained by (1) coating with surfactants, (2) NCC surface oxidation, and (3) grafting the polymer chain on the surface of the fibres (Salajková 2012).

❖ Surface chemical modification

The main goal of the NCC surface modification is to improve their compatibility with hydrophobic polymer. That can be obtained by the introduction of new negative or positive electrostatic charges on the surface of nanocellulose. Those charges increase the particle-particle repulsive forces and, consequently, improve the dispersibility of NCC in polymer matrix. Different surface modification methods, such as non-covalent surface modifications via adsorption of surfactants (Heux, Chauve et al. 2000, Bondeson and Oksman 2007, Salajkova, Berglund et al. 2012), TEMPO ((2,2,6,6-tetramethylpiperidin-1-yl)oxyl) oxidation (de Nooy, Besemer et al. 1994, Hirota, Tamura et al. 2009, Fujisawa, Okita et al. 2011, Johnson, Zink-Sharp et al. 2011, Yang, Peng et al. 2015), silylation (Look 1968), fluorescently labeled (Dong and Roman 2007) and grafting the polymer chain on the surface of NCC (Habibi, Goffin et al. 2008, Dadkhah Tehrani and Neysi 2013, Peltzer, Pei et al. 2014) have been used (see Figure 1.12).

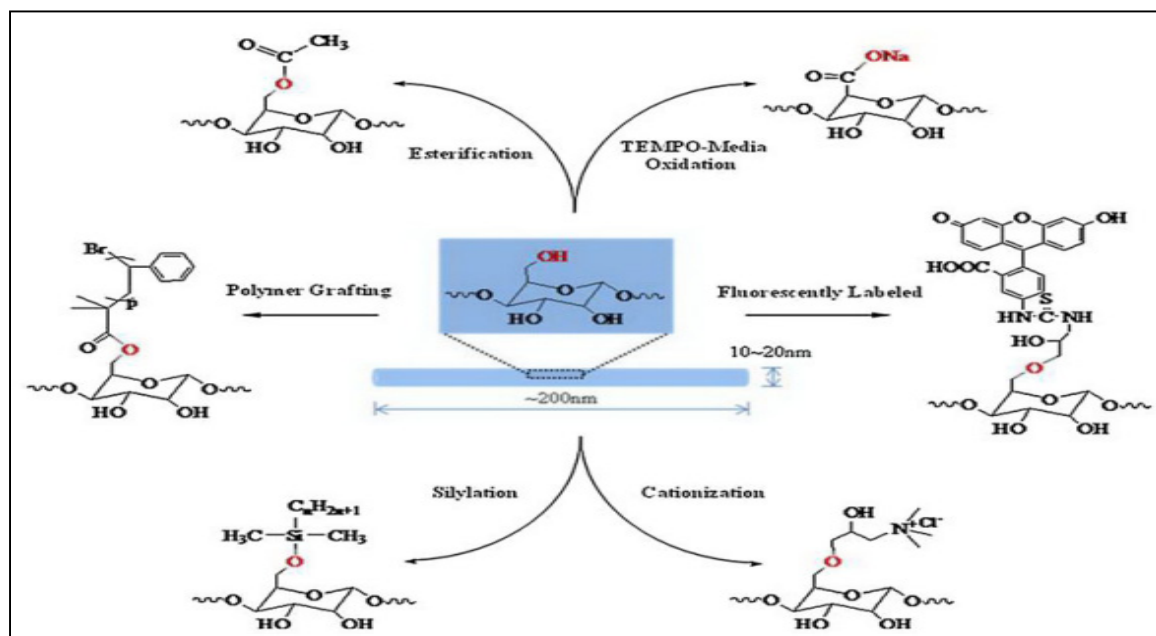


Figure 1.12 Common chemical modifications of nanocrystalline cellulose (NCC) (adopted from Peng et al.(Gousse, Chanzy et al. 2002, Habibi, Chanzy et al. 2006, Dong and Roman 2007, Hasani, Cranston et al. 2008, Braun and Dorgan 2009, Morandi, Heath et al. 2009, Peng, Dhar et al. 2011))

The increased interest for the chemical modification of NCC is explained by the increasing potential applications of modified NCC in polymer nanocomposites. In most cases of those surface treatments, an organic solvent is used, which is not environmentally friendly and is not preferred by industry. Therefore, to solve this problem, some research has been proposed to take advantage of good dispersibility of NCC in water and adding, directly, an aqueous suspension of NCC in melt compounding through liquid feeder (Aji, Ayan et al. 2006, Oksman, Mathew et al. 2006, Herrera, Mathew et al. 2015). This method requires a good stability to hydrolysis of the polymer matrix in the presence of water and high temperature. Another advantageous method is also used, particularly in case of polyolefins, involves the compatibilization of NCC nanocomposite by melt compounding with polyolefin grafted maleic anhydride or any other coupling agent.

❖ Dispersion/Coupling agents

Coupling agents are successfully used in wood plastic composites to improve adhesion, dispersion and compatibility between wood fibres and polyolefins (N/A , Yeh 2003, Li 2012). Different coupling agents, such as glycidyl methacrylate and maleic anhydride have been commonly used in polymer composites. Maleic anhydride grafted polyolefins is now a well-known compatibilizer agent used to promote strong interaction between polymer matrix and fillers. The possible hypothetical reaction chemistry of this coupling agent and cellulosic fibres is presented in the Figure 1.13.

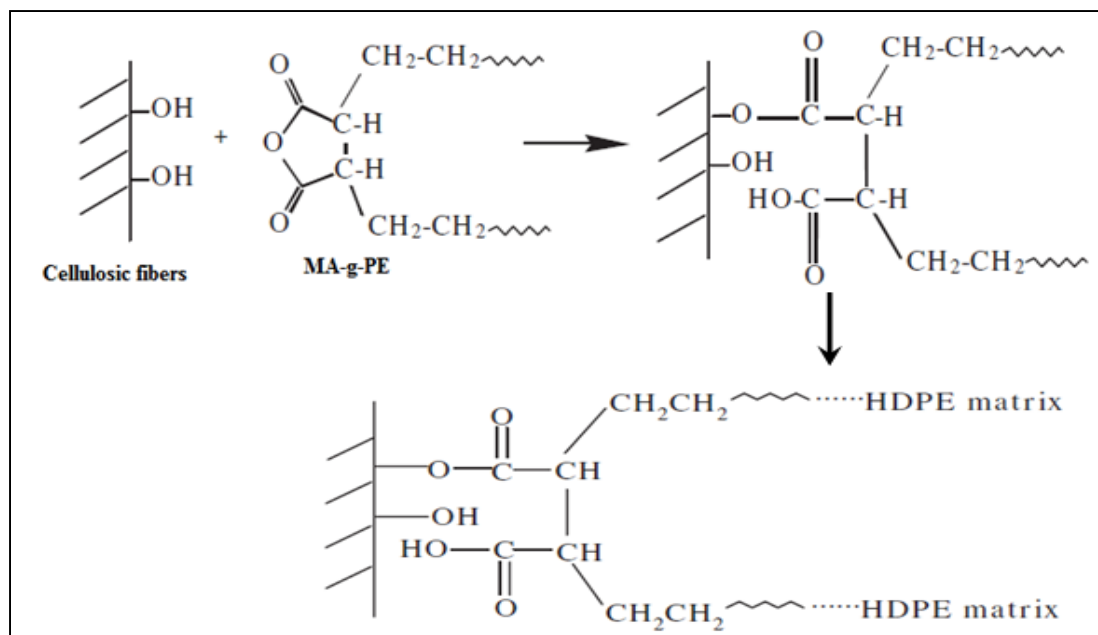


Figure 1.13 A possible mechanism of reaction between coupling agent, cellulosic fibers and HDPE (reproduced from Li, Qingxiu et al (Li and Matuana 2003))

The molecular weight and maleic anhydride content are the principal parameters affecting the effectiveness of maleic anhydride grafted polyolefin (N/A , Yeh 2003, Kulkarni and Mahanwar 2013). In fact, it has been found that increasing maleic anhydride content (or high loading of compatibilizer agent) generally improves the fiber dispersion and reduces particle-particle interaction. However, using a high level of maleic anhydride content can be detrimental to the mechanical properties of composite due to the increasing of their immiscibility with polymer matrix (N/A , Kato, Usuki et al. 1997). The same effect has been observed for maleic anhydride molecular weight. When a coupling agent with low molecular weight is used, it can result in better dispersion. Nevertheless, increasing molecular weight can provide much better improvement in mechanical properties (Kulkarni and Mahanwar 2013). Thus, it is quite important to make a good choice of coupling agent and its adding content to have an optimal compatibilizing efficiency of polymer composite.

Similar to wood fibres, maleic anhydride grafted polyolefin has been also used to improve dispersion of NCC in polymer nanocomposites. Elif Bahar et al. (Bahar, Ucar et al. 2012) examined the effects of coupling agents on the tensile properties of PP/cellulose nanowhiskers nanocomposites. They found that increasing maleated polypropylene (MAPP)

content leads to a decrease of tensile strength and increase of tensile modulus of nanocomposite. This was explained by the stronger interfacial interactions rigidity and reduced molecular mobility in the structure, which leads to an increase of fragility and decrease of strength. The same trend was observed by Matheus Poletto et al.(Poletto, Zeni et al. 2012) and Rana et al. (Rana, Mandal et al. 1998), they attributed the decrease of the mechanical properties of polypropylene/ wood composite using a high content of the compatibilizer agent to the migration of coupling agent excess around the fibre surfaces, that causes slippage of the polymer matrix. Maija Pöllänen et al.(Pöllänen, Suvanto et al. 2013) and Velmurugan Palaniyandi et al.(Palaniyandi and Simonsen 2007) also investigated the mechanical properties and morphology of HDPE/Microcrystalline cellulose composites modified with a maleic anhydride grafted polyethylene. They showed that the incorporation of compatibilizer enhanced mechanical properties of the resulting composites.

1.2.1.5 Processing of polymer nanocomposites

In the manufacturing of polymer nanocomposites, the final properties are governed by the compounding technique used to mix fibres and matrix, which will affect the orientation, dispersion and morphology of nanocomposite. Different methods have been proposed for processing of polymer/NCC nanocomposites, including melt-mixing of a dried NCC with polymer in extrusion or internal mixer, solution casting of polymer solution and NCC dispersed in an organic solvent, aqueous dispersion of NCC with a water-soluble polymer and in-situ polymerization by dispersion NCC in a monomer solution. Choosing compounding processing method depends on the polymer type, the volume of composite that we want to produce and the economic and environmental aspects.

❖ Solution blending

Solution blending (solvent casting) is the most common method used in the literature to achieve a good dispersion level of NCC in polymer matrix. In this method, NCC nanoparticles are mixed with a polymer solution involving organic solvent. Two main approaches can be adopted, solvent mixture (Long Jiang, Morelius et al. 2008, Fortunati,

Puglia et al. 2013, Corrêa, de Moraes Teixeira et al. 2014) by mixing of NCC aqueous suspension with miscible water-solvent polymer solution and solvent exchange approach (Ljungberg, Bonini et al. 2005, Siqueira, Mathew et al. 2011, Bahar, Ucar et al. 2012, Espino-Pérez, Bras et al. 2013, Abdulkhani, Hosseinzadeh et al. 2014, Fortunati, Rinaldi et al. 2014, Fortunati, Luzi et al. 2015), mostly used, by surface modification of NCC in water suspension followed by solvent exchange procedure from water to non-polar polymer solution. In the latter, the exchange of NCC suspension between water and organic solvent can be done using centrifugation process or by drying surface modified NCC before mixing with polymer solution. After solvent evaporation, nanocomposite NCC/ Polymer film can be collected. In contrast to melt blending, solution blending resulted in a better dispersion of NCC in polymer matrix. Long Jiang et al. (Long Jiang, Morelius et al. 2008) investigated the effect of melt blending and solution casting technique in the dispersion and mechanical properties of poly(3-hydroxybutyrate-co-3-hydroxyvalerate) / NCC ((PHBV)/NCC) nanocomposite. They reported that solution casting of PHBV/NCC in N, N-dimethylformamide (DMF) resulted in a good dispersion and increase of tensile properties. On the other hand, melt blending in extruder resulted in agglomeration of NCC, measuring up to 30 μm , on the surfaces of the composites. These agglomerations have negative effects by the decrease of tensile strength and modulus of polymer nanocomposites. SEM observations of PHBV/NCC surface prepared by techniques, solvent blending and melt blending, are presented in the Figure 1.14.

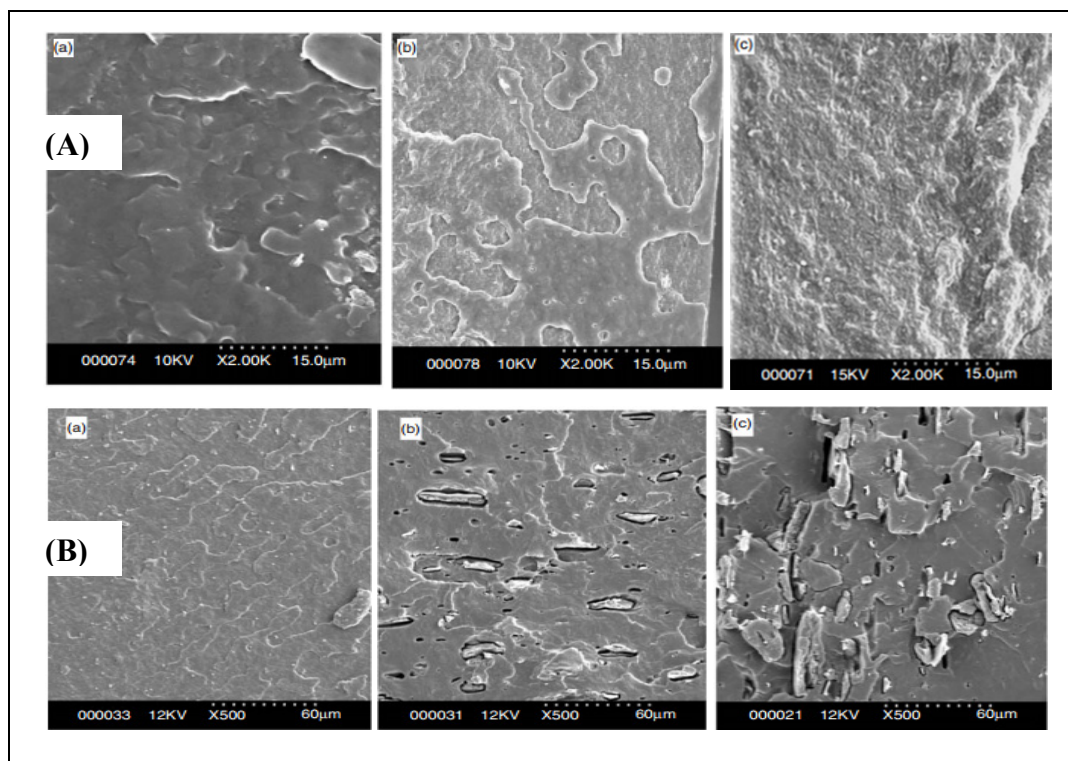


Figure 1.14 Fracture surfaces of (A) : solution-casted of neat PHBV (a), PHBV/2% CNW (b), and PHBV/5% CNW (c) composites and (B): extrusion/injection molding of neat PHBV (a), PHBV/2% CNW (b), and PHBV/5% CNW (c) (Long Jiang, Morelius et al. 2008)

Nevertheless, the use of solvent technique is confined is not preferable for industry. In fact, it has several drawbacks limiting their use for industrial scale such as: the use of environmentally unfriendly organic solvent, high cost processing (additional cost of solvent), need specific chemical devices and it can only produces in a small quantity. In addition, some polymer matrixes such as polyolefins (Ljungberg, Cavaillé et al. 2006, Bahar, Ucar et al. 2012, Peng, Gallegos et al. 2014) and polyamides(Panaitescu, Gabor et al. 2015) with high molecular weight make difficult their mixing with NCC using solution blending method due to their high resistance to most of organic solvents.

❖ **Melt mixing in internal mixer**

Melt compounding of polymer nanocomposites using internal mixer is one of the most advantageous methods widely used in the industrial scale. It is simple and doesn't need any prior specific knowledge to be used, no organic solvents are required (very advantageous in case of polyolefins which are difficult to dissolve) and able to produce a sufficient quantity for industrial applications. However, in case of polymer/NCC nanocomposite the dispersion of NCC by melt mixing is more difficult compared to solution casting methods due to the tendency of NCC to form a big agglomeration at high viscosities of the composite melt during processing. In literature the melt-mixing process has not been widely used for the compounding of polymer/NCC because of not very successful dispersion results (Oksman, Mathew et al. 2006, Bondeson and Oksman 2007, Sapkota, Kumar et al. 2015). To overcome this disadvantage, a combination of pre-mixing by solution casting and melt mixing was reported. However, this approach may lose all the advantages of melt-mixing method and draw it back to the solution casting.

The challenge of dispersion state can be strongly affected by the processing conditions and the mixing protocol. The principal parameters affecting dispersion in polymer nanocomposites are rotor speed (shear stress), mixing time and barrel temperature. In addition, the compounding steps (one-step and two-step process) may also affect the interaction between fibers and polymer if a surface modification by coupling agent was performed.

➤ **Influence of rotor speed**

The rotor speeds or shear rate of internal mixer have a significant effect in processing compounding of polymer nanocomposite. Indeed, the separation of NCC aggregates is mainly carried with shear stress provided by rotor screws. At high rotor speed, the shear stress increases resulting in an improvement of NCC dispersion. However, at an extremely high rotor speed value (very high shear stress); the degradation of NCC could result in a reduction of NCC length by mechanical damage. Janak Sapkota et al. (Sapkota, Kumar et al.

2015) investigated the influence of shear rate in the reduction of the NCC length upon melt processing. Transmission electron microscopy (TEM) images of neat NCC and NCC extracted from PVA/NCC (Polyvinyl acetate/NCC) nanocomposites made by internal mixer and twin-screw extruder was used to quantify the possible reduction of NCC length. They reported that high shear rates caused a slight reduction in length of NCC extracted from composite in comparing to neat NCC. This microscopic observation was confirmed by the decrease in mechanical properties due to NCC reduction length. Figure 1.15 shows the effect of shear rate on the storage modulus of PVA/NCC nanocomposites.

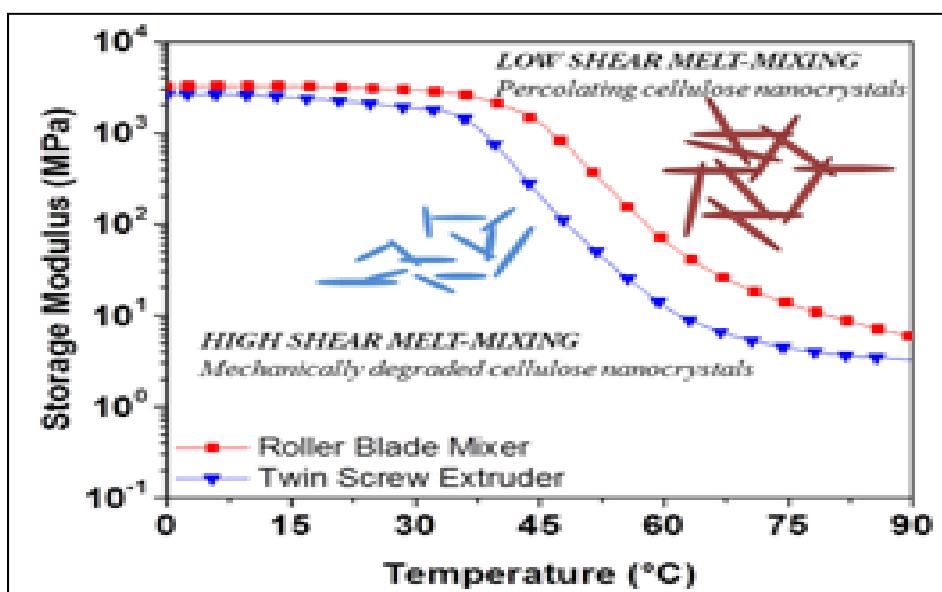


Figure 1.15 Effect of shear melt-mixing stress in storage modulus of poly(vinyl acetate) (PVAc)/Nanocrystalline cellulose (NCC) nanocomposite (Sapkota, Kumar et al. 2015)

A similar outcome was reported by R. Andrews et al. (Andrews, Jacques et al. 2002) for melt-mixing of carbon multiwall nanotube/ polymer nanocomposites. On the other hand, using low shear rate can lead to the agglomeration of NCC and difficulties in achieving the desired dispersion (Sapkota, Jorfi et al. 2014). The optimum rotor speed in an internal mixer reported in the literature for cellulose nanocomposite was around 50 to 60 rpm depending on polymer molecular weight, processing temperature and the mixer chamber

volume(Ljungberg, Cavaillé et al. 2006, Peng, Gallegos et al. 2014, Kamal and Khoshkava 2015).

➤ **Influence of mixing time**

In internal mixer, mixing time of polymer nanocomposites was regarded, in addition of rotor speed, as a very important parameter to improve dispersion of fillers. Longer mixing time increases the diffusion mechanism of nanofillers in molten polymer chains and provides sufficient time for breaking nanoparticle aggregations(Moghri, Shahabadi et al. 2013). However, at very long mixing time thermal oxidation contributes to the degradation of nanofillers and polymer and result in a negative effect on mechanical properties of composite. This degradation effect is more critical in the case of natural fibres such as NCC (degradation above 200°C) (E.Jakab, O.Faix et al. 1997, RINGUETTE 2011)) and some polymers which are sensitive to thermal degradation. Mixing time and rotor speed should be combined together to have better dispersion improvement without much degradation of polymer and filler reinforcement effect. In fact, to avoid this degradation increase rotor speed must be accompanied by the reduction of mixing time, as well as at long mixing time, the rotor speed (shear stress) must be lower (O. Ujianto 2015). Choosing residence times should be based also on observation of the torque in the mixer. Stabilized torque gives a precise indication if the homogenous dispersion was reached(El-Shekeil, Sapuan et al. 2013).

➤ **Influence of set temperature**

The processing temperature to melt compounding of nanocomposites based NCC is a critical parameter. At a high set temperature the viscosity of polymer is much lower which should make the diffusion and dispersion of NCC in the polymer chains easier. However, on the other hand, increasing temperature can result in a decrease of shear stress level applied during mixing, thermal degradation of NCC (degradation above 200°C) (E.Jakab, O.Faix et al. 1997, RINGUETTE 2011) and decrease of mechanical properties of nanocomposite(El-Shekeil, Salit et al. 2011, El-Shekeil, Sapuan et al. 2013). In order to reduce the effect of temperature on the natural fiber thermal degradation a general trend is to avoid the synergistic effect of moisture and temperature by fiber drying step before processing.

However, this is not possible in the case of NCC due to their agglomeration tendency by forming very strong hydrogen bonding between the hydroxyl groups (Nakamura, Hatakeyama et al. 1981, Peng, Gardner et al. 2012). In addition, during the extraction stage of NCC by sulfuric acid hydrolysis treatments the formation of sulfate groups at the surface lead to a decrease thermal stability (from 250 to 125 ° C) (Cho, Park et al. 2013, Lin and Dufresne 2014).

➤ **Influence of processing steps**

The compounding process of natural fibers with polymer composite can be performed in one step or two step process (master-batch). In one-step process the aim is typically to produce a homogeneous mixture without giving importance to the dispersion such as pre-mixing step prior to extrusion or injection. Contrariwise the master-batch method is widely used in the polymer processing industry, with internal mixer, as a comprehensive step for preparing the composite. In the latter, a high content of fillers is firstly compounded with coupling agent (master-batch) to improve their compatibility, followed by dilution of master-batch with neat polymer in a second mixing step. The two step method using master-batch method resulted in better dispersion and better mechanical properties than direct mixing (Krzysik and Youngquist 1991, Lu, Wu et al. 2004, Peng, Gallegos et al. 2014, Ma, Zhang et al. 2015). For NCC nanocomposites the master-batch step is typically prepared in solution blending or a prior step by melt blending in an internal mixer before extrusion (Gong, Pyo et al. 2011, Arrieta, Fortunati et al. 2014, Ma, Zhang et al. 2015). This can be explained by the low thermal stability of NCC and the difficult of dispersion in mixer. To our knowledge, there are no studies in the literature that has investigated the effect of both master-batch and direct mixing of polymer /NCC in internal mixer.

1.2.1.5.1 Liquid feeding

Nanocrystalline cellulose derived from acid hydrolysis presents a very good dispersion in water and some medium solvents suspension due to abundance of negative charges in their surfaces (anionic sulfate ester groups)(Dufresne 2013). Taking advantage of this property, melt compounding of NCC nanocomposites can be produced using liquid feeding method.

Prior to the extrusion, NCC suspension (water or ethanol) is prepared and pumping directly on the molten polymer during processing. Lowest quantity of appropriated liquid and atmospheric venting pump must be used to make easier the evaporation of liquid and do not deteriorate the polymer matrix properties. Giovanni Roggio(Roggio 2014) studied the compounding of PLA/NCC nanocomposites using liquid feeding in extrusion. Freeze dried NCC and wet NCC was dispersed in triethyl citrate (TEC) plasticizer and ethanol, then the suspension is pumping in melt PLA using liquid feeder. They reported that the use of water in the feeding suspensions improves the dispersion of NCC in the PLA matrix and resulted in better mechanical properties of nanocomposite compared to freeze dried NCC. At 5 wt. % of NCC suspension content the tensile modulus and tensile strength of PLA/NCC nanocomposite increased by 68% and 35% respectively compared to neat PLA. However, a decrease of tensile strength and modulus was observed when 5 wt. % of freeze dried NCC was used.

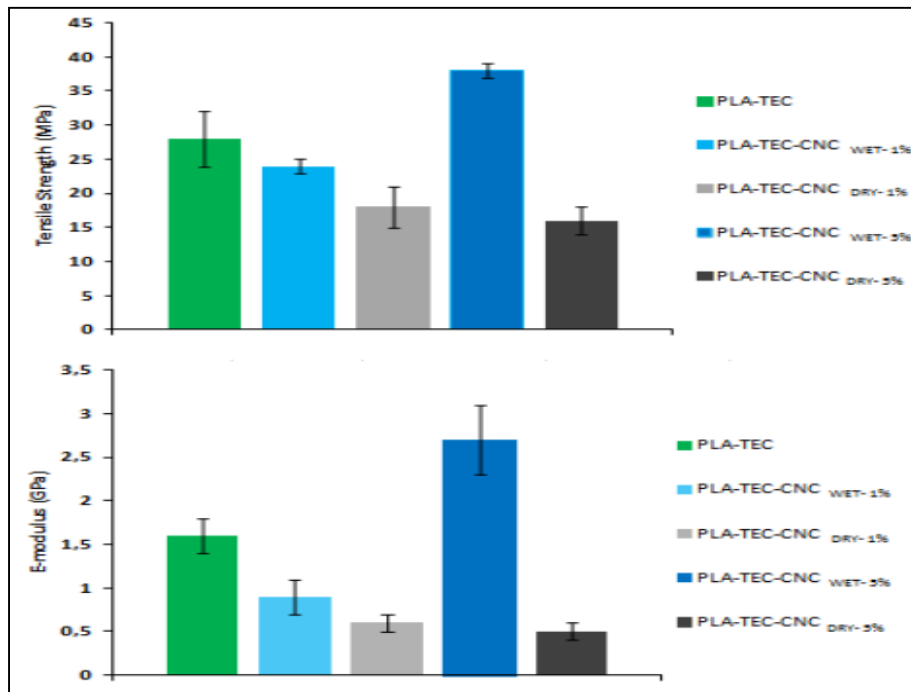


Figure 1.16 Mechanical properties of PLA/NCC nanocomposites using different processing methods and NCC content (Roggio 2014)

A similar result was reported by D. Bondeson et al. (Bondeson, Syre et al. 2007) using cellulose acetate butyrate (CAB) as a matrix. Upon addition of 5 wt. % NCC in TEC suspension, the tensile modulus and tensile strength increased by 300% and 100%, respectively, compared to neat CAB. However, a decrease of mechanical properties compared to neat PLA was shown by K. Oksman et al. (Oksman, Mathew et al. 2006) using a suspension of NCC with N,N- Dimethylacetamide (DMAc) and Lithium chloride (LiCl) as swelling agent and Polyethylene glycol (PEG) as a plasticizer. This negative effect has been explained by the degradation of PLA properties with additives using in NCC suspension. So a successful process requires a good choice of NCC suspension liquid not only to improve the dispersion of NCC in a molten polymer but also to avoid the degradation of polymer properties.

Recently, the demonstrated success with the liquid feeding process of NCC suspension encouraged Natalia Herrera et al. (Herrera, Mathew et al. 2015) to prepare, for the first time, PLA nanocomposite based cellulose nanofibers (NFC) suspension with glycerol triacetate (GTA). They reported the same results with a good dispersion of NFC and increase of mechanical properties of PLA/NFC nanocomposite.

1.2.2 Potentiality of using nanofillers in HDPE nanocomposites

Reinforcement of nanocomposite with organic and inorganic nanoparticles has been reported in the literature by many researchers. Indeed, a good improvement of polymer properties can be achieved with typically 3 to 10 wt.% nanoparticles such as clays, carbon nanotubes and nanocrystalline cellulose (Wang 2008, Islam, Masoodi et al. 2013). Therefore, many investigation studies have been carried to understand the effect of addition of nanoparticles on the mechanical and physical properties of polymers.

Regardless of their size and shape, the addition of nano or microfillers in a polymer matrix has, in general, a positive effect on increasing tensile modulus and strength of composite. This enhancement is governed by the interfacial interaction between polymer and fillers, dispersion, concentration, aspect ratio and orientation of fillers (Chevigny, Jouault et al. 2011, Islam, Masoodi et al. 2013, Pedrazzoli, Pegoretti et al. 2015). In fact, it was reported in many works that, when a good dispersion was achieved, increasing the volume fraction of

nanoparticles can increase the Young modulus and flexural modulus of neat matrix (Utracki , Aït Hocine 2010). However, on the other side, the tensile strength, flexural strength and impact resistance remain constant or in some cases decrease as weight fraction of NCC increases. These results can be explained by the most critical effect of agglomeration when a high nonlinear deformation stress is applied during the test. These stress tension forces are lower at the beginning of the test, where the modulus is measured, that is why the stress-transfer across the filler–matrix interface doesn't have the same effect between modulus and strength resistance (Aït Hocine 2010, Panaitescu, Radovici et al. 2011).

For HDPE nanocomposites, such behaviour of mechanical properties was observed by using various nanofillers such as nanoclay (A. Pegoretti 2007, Tjong and Bao 2007, Carrera, #xed et al. 2013, Hamid, Akhbar et al. 2013), carbon nanotubes (Kim, Hong et al. 2009, Vega, Martínez-Salazar et al. 2009), TiO₂ (Panaitescu, Radovici et al. 2011), nano-SiO₂ (Zhang, Rong et al. 2003) or nanocrystalline cellulose (Palaniyandi 2004, Li, Song et al. 2014, Nihat Sami ÇETİN 2015). In these studies, it was assisted that the values of Young's modulus and tensile strength can increase by 10% to 50% and 10% to 26%, respectively, compared to neat polymer. It was also shown that there exists a critical concentration of nanoparticles in which there is a decrease of modulus due to agglomeration phenomena.

Cheng Zhu Liao et al. (Liao and Tjong 2012) reported an increase in tensile stress and Young's modulus of HDPE with the increase of alumina nanoparticles content up to 6%. However, the improvement obtained is inconsiderable and does not exceed 10% compared to the neat polymer. M. Trujillo et al. (Vega, Martínez-Salazar et al. 2009) found that the addition of only 0.52 wt.% MWNT improve tensile modulus of HDPE by almost 100% without decreasing their ductility.

According to our literature review, the effect of nanoparticles on flexural properties of polymer nanocomposites was not very discussed in the literature (Sinha Ray 2013). Omar Faruk et al. (Faruk and Matuana 2008) report the effect on flexural strength and modulus of injection molded HDPE reinforced with five different types of nanoclays (5% content). Table 1.1 summarizes their results for flexural strength and modulus. The results show an increase of flexural modulus for all types of cloisite with more than 41% in case of Cloisite 10A.

However, except for Cloisite 10A (increasing by 25%) no significant effect was observed for all other nanoclay.

Table 1.1 Influence of nanoclay types on the flexural properties of nanoclay/HDPE nanocomposites (Faruk and Matuana 2008)

Types of nanoclay in HDPE matrix	Chemical structure of the nanoclays	Flexural properties	
		Strength (MPa)	Modulus (MPa)
None (control)	-	25.3 ± 1.4	667 ± 61
Cloisite 10A	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3 - \text{N}^+ - \text{CH}_2 - \text{C}_6\text{H}_5 \\ \\ \text{HT} \end{array}$	31.7 ± 1.8	947 ± 76
Cloisite 15A	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3 - \text{N}^+ - \text{HT} \\ \\ \text{HT} \end{array}$	24.7 ± 0.8	693 ± 40
Cloisite 20A	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3 - \text{N}^+ - \text{HT} \\ \\ \text{HT} \end{array}$	26.4 ± 0.5	757 ± 35
Cloisite 25A	$\begin{array}{c} \text{HT} \\ \\ \text{CH}_3 - \text{N}^+ - \text{CH}_2\text{CH}(\text{CH}_2)_8\text{CH}_3 \\ \\ \text{CH}_3 \end{array}$	26.8 ± 0.6	759 ± 21
Cloisite 30B	$\begin{array}{c} \text{CH}_2\text{CH}_2\text{OH} \\ \\ \text{CH}_3 - \text{N}^+ - \text{T} \\ \\ \text{CH}_2\text{CH}_2\text{OH} \end{array}$	25.7 ± 0.3	± 19

1.2.3 Hybridization effect of nanoparticles on WPC

Wood fibers have long been used in thermoplastic polymers to make composites with good mechanical and physical properties. However, generally, the characteristic properties, such as flexural, tensile, impact and water absorption properties of WPC are affected by the poor interfacial adhesion between hydrophilic fibers and hydrophobic polymer. This makes it difficult to have a good stress transfer between the two components and deteriorate, consequently, the composite performances. Several efforts have been made to find some

solutions to overcome the limitations of WPC. One way is to do surface modification of fibers or adding coupling agent to reduce their surface tension. Another solution, also reported in the literature consists of adding small amounts of nanofillers to increase the interphase volume and interfacial interaction between fibers and matrix. In particular, NCC have a good mechanical properties, high surface area and high aspect ratio ($L/d > 30$) what makes them a good candidate for hybrid WPC. In this section we will summarize the progress research in the use of nanofillers for WPC manufacturing, and the effect of adding nanofillers (in particular NCC) on the mechanical and physical properties of wood plastic composites.

1.2.3.1 Mechanical properties

The major defect of WPC is their lower flexural and tensile strength resulting from poor interfacial adhesion between matrix and wood fillers. Enhancing mechanical properties of WPC can be performed by the incorporation of nanofillers into hybrid nanocomposite to improve interfacial interactions. The hybridization of WPC with some nanofillers such as carbon nanotubes, nanoclay and nanocrystalline cellulose have shown various mechanical behaviors. Some studies reported encouraging mechanical results when nanofillers are added, although, many other researchers found a decrease of mechanical properties when studying hybrid nanocomposites. This can be mainly explained by the degree of nanoparticles dispersion, nanofillers loading and polymer matrix type.

To our knowledge, there are no studies that examined the effect of hybridization of WPC by nanocrystalline (NCC) cellulose. However, some limited studies in the literature reported the effect of combining microcrystalline cellulose (MCC) (sizes greater than 500 nanometers) and wood flour in polymer composite. Alireza Ashori et al (Ashori and Nourbakhsh 2010) investigated the effect of adding microcrystalline cellulose (MCC) on flexural and tensile strength on PP/wood composite. They reported that partial replacement of wood flour by 8 % MCC can significantly improve the mechanical properties compared to composite without MCC. A. Nourbakhsh et al. (Nourbakhsh, Ashori et al. 2010) reported an increase of tensile and flexural properties of PP/wood flour composite when 4 wt.% of microcrystalline

cellulose (MCC) was used. They also reported a better effect of MCC in WPC performances compared to nanoclay at the same nanoparticles loading. The maximum improvement was obtained when 8 wt. % MCC and 3 wt. % of nanoclay was incorporated in WPC composite. Compared to control sample (PP/wood/MAPP), tensile strength and modulus were increased by 12% and 55%, respectively. Also, flexural strength and modulus were presented a significant enhancement by 25 % and 20 %.

In the literature review, nanoclay was mostly studied as reinforcement nanofillers for hybrid WPC. This may be due to lower cost and easier control of its surface chemistry compared to other nanoparticles.

Hasan Ziaei Tabari et al. (Tabari, Nourbakhsh et al. 2011) have examined the effect of adding 3 w% nanoclay (Cloisite Na+) on the mechanical properties of PP/ wood flour composites. Maleic anhydride was also added to the composite to improve adhesion between fillers and PP. An improved tensile and flexural strength and modulus were observed (see in Table 1.2).

Table 1.2 Effect of addition maleic anhydride and clay concentration on the mechanical properties of polypropylene /wood flour composite (Tabari, Nourbakhsh et al. 2011)

		Tensile strength (MPa)	Tensile Modulus (GPa)	Flexural strength (MPa)	Flexural modulus (GPa)
PP+40w% wood flour + 2,5% MA	0% nanoclay	32,9	2,5	40,3	2,4
	3% nanoclay	38,7	3,3	48,8	2,7
PP+40w% wood flour + 5% MA	0% nanoclay	36,7	3,1	47,7	2,6
	3% nanoclay	39,6	3,9	50,6	2,9

The same enhancement result of mechanical properties was reported by Yang Zhong et al (Zhong, Poloso et al. 2007), Yong Lei et al (Lei, Wu et al. 2007) and Ishagh Babaeia et al (Babaei, Madanipour et al. 2014) when a small amount of nanoclay (less than 3 %) was added to HDPE/wood plastic composite. In all these studies, a good dispersion of nanoclay is

required to have the synergistic effect between the different fillers incorporated in polymer matrix. Therefore, a maleic anhydride is usually used to improve nanoclay exfoliation and compatibility with hydrophobic polymer.

The morphology and type of nanoparticles present also a significant effect on the hybrid wood plastic composite. For example, Omar Faruk et al. (Faruk and Matuana 2008) studied the effect of five different organically modified nanoclays for the improvement of mechanical properties of HDPE/wood/nanoclay nanocomposite. First, the nanoclays were used with neat HDPE to increase their stiffness and identify the most effective nanoclay type on wood-plastic composites. Then, HDPE/cloisite10A nanocomposite was used as a matrix in the compounding of wood composite. Cloisite 10A has proven the best enhancing of both flexural and tensile properties. This is due to the good dispersion of Cloisite 10A compared to other nanoclay types. Figure 1.17 showed the TEM image of different cloisite dispersion. It can be clearly seen that the good dispersion of Cloisite 10A compared to other nanoclay resulted in a significant increase of mechanical properties.

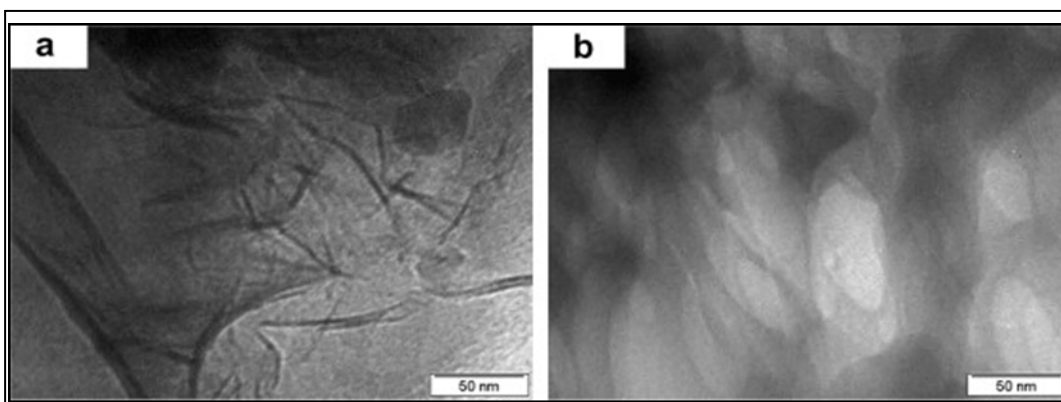


Figure 1.17 TEM of HDPE/nanoclay composites: (a) Cloisite 10A nanoclay and (b) Cloisite 15A nanoclay (Faruk and Matuana 2008)

Trying to reach better optimization of hybrid wood plastic composite performance, many researchers have examined the effect of high nanoclay content on the mechanical properties of wood composite. They reported that increasing the amount of nanoparticles above a critical value could reduce their dispersion in a polymer matrix and deteriorate the mechanical properties of composite.

Behzad Kord et al. (Kord 2011) suggested that adding up to 2 phc nanoclay can improve the tensile modulus and strength of HDPE/rice husk flour composite. However, when the concentration of nanoclay exceeds 4 phc, a decline of mechanical properties can be observed. This result was attributed to the formation of nanoclay agglomeration.

Ishagh Babaei et al (Babaei, Madanipour et al. 2014) reported an increase of tensile modulus and strength of HDPE/wheat straw flour by adding up to 2% of exfoliated nanoclay. Nevertheless, the lack of dispersion when 5% of nanoclay loading was used, leads to a significant decrease of the mechanical properties of composite. Many other researchers using polypropylene as a matrix also confirmed this negative effect of adding a large quantity of nanoparticles and they are all returned the deterioration of mechanical properties to the lack of nanoparticles dispersion (Nourbakhsh and Ashori 2009, Hemmasi, Khademi-Eslam et al. 2010, Yeh and Gupta 2010, Kord 2012).

Carbon nanotube was also used to improve mechanical properties of wood plastic composite. Hamed Younesi Kordkheili et al. (Kordkheili, Farsi et al. 2013) was using carbon nanotubes compounding in an internal mixer with low density polyethylene and wood flour. High aspect ratio and large surface area of carbon nanotube caused an increase of mechanical properties of the composites. Flexural modulus and strength were increased by increasing carbon nanotube content (0, 1, 2, 3 phc) while the highest impact resistance was obtained at 2 phc due to the agglomeration of nanoparticles at high concentration level. The mechanical results were explained by morphological study using SEM micrographs of fractured samples. It has been proved that adding carbon nanofillers increase interfacial adhesion between wood and PP (Kordkheili, Farsi et al. 2013).

Zhang et al. (Zhang, Zhang et al. 2009) reported a decrease by 5% of flexural modulus when 1 wt. % of carbon nanofibers was introduced in PP/ wood fibers. The SEM observation indicates that this reduction of mechanical properties is attributed to the poor dispersion of carbon nanofibers.

From the results presented above, it can be concluded that a synergism between the addition of nanofillers and wood fibers can be obtained only when a good dispersion was achieved. Otherwise, a decline of mechanical properties can be observed, particularly, when higher nanoparticles loading is used.

1.2.3.2 Physical properties

In addition, of mechanical properties enhancement, incorporating nanoparticles in wood plastic composite was provided a good ability to reduce swelling and water absorption of composite. This presents a promising opportunity to overcome limited moisture resistance of wood composite. Thermal stability, fire retarding properties and electrical conductivity of WPC can be also improved when an appropriate amount of nanoparticles is introduced.

Hasan Ziaei Tabar et al (Tabari, Nourbakhsh et al. 2011) report improved hygroscopic properties of a PP/wood flour composite with 3% nanoclay loading. This result was attributed to the ability of nanoclay to block the void spaces in WPC composite and prevent, consequently, water penetration. Another observation was reported by Ismaeil Ghasemi and Behzad Kord (Kord 2009) suggested that the reduction of water absorption is mainly due to the hydrophilic nature of nanoclay which prevent water migration to the polymer matrix. However, the agglomeration of nanoparticles by increasing nanoclay concentration caused the increase of water absorption (Supri AJ 2008, Gu, Kokta et al. 2010). Some other authors such as Behzad Kord (Kord 2012) observed that adding nanoclay leads to decrease of water absorption and thickness swellings.

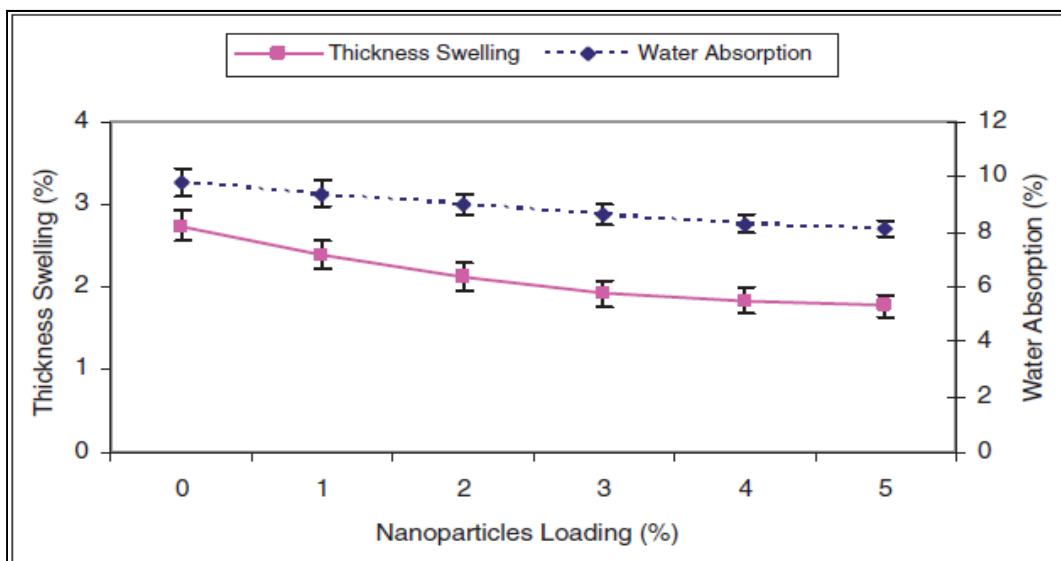


Figure 1.18 Effect of nanoclay loading on water absorption and thickness swelling of PP/ hemp fibers composites(Kord 2012)

This can be explained by the good exfoliation of nanoclay obtained in composite. So such improvement of moisture resistance of hybrid composite requires good nanoparticles dispersion state.

Although, carbon nanotube is used to improve mechanical properties and electrical conductivity of polymer composite, their effect on the water absorption behavior of hybrid wood composite was investigated. Hamed Younesi Kordkheili et al. (Kordkheili, Farsi et al. 2013) showed a decrease of water absorption and thickness swelling of LDPE/ wood flour when the concentration of carbon nanotube increase up to 3wt.%.

As has been observed for mechanical properties, enhancing moisture resistance of hybrid nanocomposite can be achieved only when a homogeneous dispersion is obtained.

1.3 Conclusion

In chapter 1, we presented an overview of nanocomposites reinforced cellulose nanocrystalline (NCC) and the potential of using nanoparticles on mechanical properties of composite. It has been observed that adding a small amount of nanoparticles, having a large surface area and high strength, can improve significantly the mechanical and physical properties of nanocomposite. However, at high nanoparticles loading, obtaining a proper dispersion by melt mixing still remains a challenge as polyolefins are hydrophobic and NCC are hydrophilic. So, we focused on the key challenges of NCC dispersion and the main strategies adopted to overcome this problem. Using compatibilizer agent such as maleic anhydride to improve nanoparticles dispersion showed encouraging results in various studies. In addition, several studies investigated the incorporation of nanoparticles such as nanoclay and carbon nanotube in wood plastic composite. They provided that a successful effect on the enhancement of mechanical and physical can be obtained. But, to our knowledge, there are no study examined the effect of NCC in wood plastic composite.

In this framework, the objective of our study is to investigate the effect of adding NCC as compatibiliser on mechanical properties and water uptake of hybrid wood plastic composite based HDPE. This hybrid composite could be used in similar applications than the WPC, i.e in construction, automotive and sport.

The following table presents the role of each component in the hybrid composite.

Table 1.3 The main role of each composite component

Component	Role
HDPE	Matrix of composite
Wood flour	Reinforcement to increase mechanical and physical properties of composite
NCC	Help to improve the compatibility between wood flour and HDPE (increase the interface interactions)
Compatibilizer agent	Improve the compatibility between wood flour and HDPE and the dispersion of NCC

CHAPTER 2

MATERIALS AND EXPERIMENTAL METHODS

This chapter presents the materials and experimental methods used in this project. First the polymer, the fillers and the compatibilizers used are presented. The processing methods are then described and characterization explained.

2.1 Technical data of the materials

This section presents the different materials that were used to manufacture the composites obtained in the project.

2.1.1 High-density polyethylene (HDPE)

High-density polyethylene (HDPE) with a melt flow index rate of 4.9 g/10 min (190°C/2.16 kg) and density of 0.960 g/cm³ was supplied by NOVA Chemicals Company in Canada as a commercial grade **SCLAIR® 2907**.



Figure 2.1 HDPE SCLAIR® 2907

2.1.2 Fillers

2.1.2.1 Nanocrystalline cellulose (NCC)

The nanocrystalline cellulose (NCC) was purchased at the Process Development Center of the University of Maine (Orono, Maine, USA)(University of Maine). It was used as a filler of nanocomposite, without any modification. The samples of NCC are in a freeze-dried form and manufactured at the U.S. Forest Products Laboratory (FPL). The dimensions and specifications of NCC source are not available.



Figure 2.2 Freeze-drying NCC

2.1.2.2 Wood flour and sisal

For composite and hybrid nanocomposites, we used the wood flour (WF) supplied by P.W.I. Industries Inc. The particle size of wood was 70 microns. The Wood flour was extracted from maple trees of Canada. Sisal short fibers were received from Brazil but, unfortunately, no data were as found or could be obtained for the Sisal.

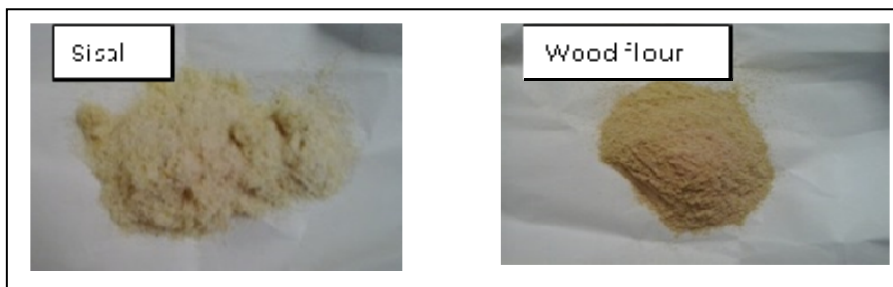


Figure 2.3 Sisal fiber and wood flour

2.1.3 Compatibilizer

The problem of adhesion between the hydrophilic fibers and hydrophobic polymers and the difficulty of filler dispersion in the polymer are the main challenges to be solved. In this regard, two grades of polyethylene-graft-maleic anhydride (PE-g-MAH) were used as coupling agent to improve the compatibility between the HDPE matrix and NCC. This compatibilizer was supplied by DuPont here called (CA1) with melt flow rate (190°C/2.16kg) 25 g/10 min and (CA2) with melt flow rate (190°C/2.16kg) 12 g/10 min.



Figure 2.4 Compatibilizer agents CA1 and CA2

2.2 Methods of preparation and characterization of samples

In this section we will present the different pieces of equipments and processes that have been used to prepare and characterize the composites based on HDPE and cellulosic fillers (NCC, wood flour and Sisal). First, the different samples were compounded in internal mixer using appropriate conditions. Then, the mixture was reduced into smaller and irregular granules using a mechanical grinder machine. Finally, the various specimens for mechanical tests were prepared according to the standardized dimensions using an injection molding machine. To evaluate the performance of different materials obtained, we studied the mechanical properties in bending, tensile and impact using a MTS machine and impact pendulum. The morphology of the samples was evaluated using scanning electron microscopy (SEM) to understand the mechanical properties of the samples. The mechanical properties were then explained in light of the morphology of the samples.

2.2.1 Compounding processes for the HDPE composites

NCC, wood flour and sisal were compounded with HDPE in a Thermo Scientific™ HAAKE™ Rheomix Lab Mixers OS 3000. The internal mixer is shown in Figure 2.5. The technical specification of the apparatus for the Haake Rheomix 3000 OS are presented in Table 2.1. Mixing conditions could be programmed through the PolyLab OS software system by setting the duration of mixing (min), temperature of mixing chamber (°C) and speed of rotors (rpm).

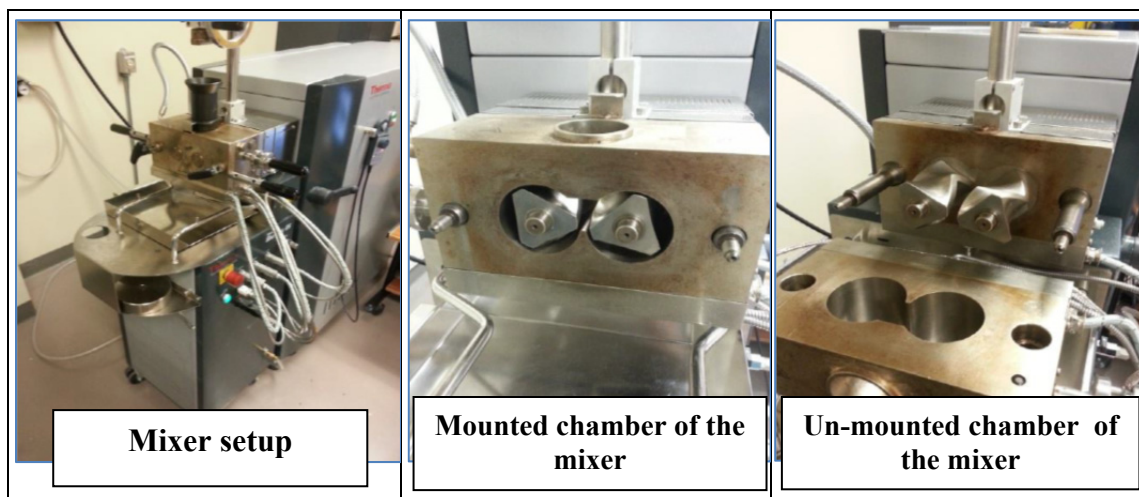


Figure 2.5 Haake Rheomix OS 3000

Table 2.1 Haake Rheomix 3000 OS technical data (Altun, Doğan et al. 2013)

Item	Technical Specifications
Total chamber volume	625 cm ³
Net chamber volume w/ rotors	310 cm ³
Max. rotor speed	250 rpm
Max. temperature:	400°C (opt. 500°C)
Max. torque:	300 Nm
Electric heating zones:	3
Air cooling zones:	3
Gear ratio	3:2

Before mixing the materials, we had to determine the quantity in grams to be fed into the Haake Rheomix 3000 OS. Equation 1 was used to determine that quantity:

$$m_c = \rho_c \cdot V_n \cdot F \quad (2.1)$$

Where, m_c is the mass of the composite compound in grams, ρ_c is the density of the composite compound in g/cm³, V_n is the net chamber volume w/rotors was equal to 310 cm³ and F is the fraction of the net chamber volume w/ rotors, which was set to be 0.65.

The melt-molding processes used for manufacturing the HDPE/NCC nanocomposites and composites based wood flour and sisal were one-step and two-step following what is shown Figure 2.6.

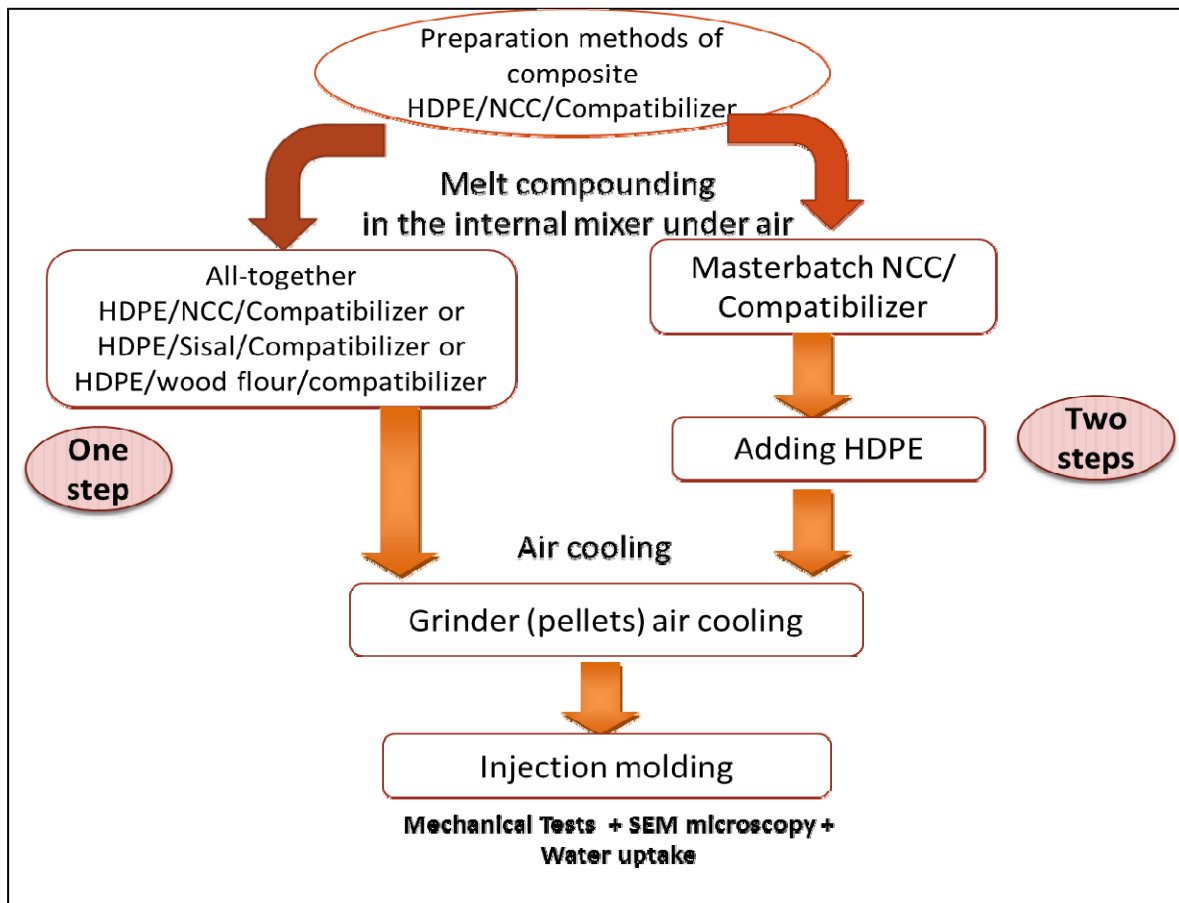


Figure 2.6 Melt-molding processes used for manufacturing HDPE composites

For the one step process, NCC was compounded with HDPE in internal mixer at 160 °C for 15 mins. The rotor speed was set at 50 rpm and the maximum temperature reached during compounding was 170 °C. In order to ensure complete blending, the mixing chamber was preheated to 160°C. HDPE was inserted first inserted in the mixing chamber. NCC was added after 4 minutes once HDPE was already molten. The same procedure was used to prepare all the nanocomposites. The compatibilizers, CA1 and CA2 were mixed together with HDPE in the case of one-step process and separately (under nitrogen atmosphere) with NCC (a masterbatch) prior to compounding in the batch mixer with HDPE. Table 2.2 summarizes the different processing parameters used for obtaining HDPE/NCC/Compatibilizer mixtures.

Table 2.2 Experimental design for compounding conditions HDPE/NCC

Test	Code/composition	HDPE (wt.%)	NCC (wt.%)	CA1 (wt.%)	CA2 (wt.%)	Processing conditions
1	HDPE	100	0	0	0	One step
2	HDPE-CA1_3	97	0	3	0	
3	HDPE-CA2_3	97	0	0	3	
4	HDPE-NCC10	90	10	0	0	
5	HDPE-NCC10-CA1_1	89	10	1	0	
6	HDPE-NCC10-CA2_1	89	10	0	1	
7	HDPE-NCC10-CA1_3	87	10	3	0	
8	HDPE-NCC10-CA2_3	87	10	0	3	
9	HDPE-NCC3-CA1_3_one step	94	3	3	0	
10	HDPE-NCC3-CA1_3_two step	94	3	3	0	Two steps
11	HDPE-NCC10-CA1_10	80	10	10	0	

Other composites containing wood flour or sisal were also obtained for the sake of comparison. Table 2.3 summarizes the experimental conditions used for the obtention of these composites.

Table 2.3 Experimental design for compounding conditions of composite and hybrid nanocomposite HDPE/NCC /wood flour or sisal

Test	Code/composition	HDPE (wt.%)	NCC (wt.%)	Wood flour (wt.%)	Sisal fiber (wt.%)	CA2 (wt.%)	Processing conditions
1	HDPE	100	0	0	0	0	One step
3	HDPE-CA2_3	97	0	0	0	3	
8	HDPE-NCC_10-CA2_3	87	10	0	0	3	
12	HDPE- WF_30	70	0	30	0	0	
13	HDPE- WF_30-CA2_3	67	0	30	0	3	
14	HDPE-WF_20-NCC_10	70	10	20	0	0	
15	HDPE-WF_20-NCC_10-CA2_3	67	10	20	0	3	
16	HDPE-Sisal_30	70	0	0	30	0	
17	HDPE-Sisal_30-CA2_3	67	0	0	30	3	

At the end of mixing process the material obtained presented the form of rigid balls (air cooling) and had to be grinded into smaller and irregular granules using a mechanical crusher machine to facilitate the injection molding process of the composite. The grinder used for that purpose was a Granu-Grinder batch granulator for laboratory supplied by Brabender CWB (shown Figure 2.7).



Figure 2.7 Granu-Grinder Granulator

The technical specifications of grinder are summarized in the Table 2. 4.

Table 2.4 Granu-Grinder technical data(Julson, Subbarao et al. 2004)

Item	Technical Specifications
Power	1.8kW
Motor Speed	1720 RPM
Feed Opening (Wx L)	127mm x 247.7mm (5" x 9.75")
Power Requirements	230 V, 60 Hz, 7.8 Amp, 3-Phase

2.2.2 Manufacture of the HDPE composites

The crushed composite compound was then injection molded using two types of injection molding machines: Arburg 370A (600 kN) for samples 2,3,5,6 and 8 and SE280HDZ machine for samples 1, 4, 7,9,10 and 11 to17 (shown in Figure 2.8). The injection molding

process conditions for every machine are summarized in Table 2.5 and 2.6. The different composites were injection molded into tensile specimens Type I according to ASTM D638-10, flexural specimens according to ASTM D790-10 and impact specimens according to ASTM D256-12.



Figure 2.8 Injection molding machines: (A) SE280HDZ and (B) Arburg 370A

Table 2.5 Experimental conditions for SE280HDZ injection molding machine

Item	Experimental Conditions
Barrel temperature (°C)	160-165-170-180
Mold temperature (°C)	30
Injection speed (rpm)	100
Cooling time (s)	25
Back pressure (MPa)	50
Injection pressure (MPa)	110

Table 2.6 Experimental conditions for Arburg 370A injection molding machine

Item	Experimental Conditions
Barrel temperature (°C)	200-200-200-200
Mold temperature (°C)	15
Injection speed (rpm)	200
Cooling time (s)	17
Back pressure (MPa)	55
Injection pressure (MPa)	90

2.2.3 Characterization of Composite

2.2.3.1 Mechanical properties

2.2.3.1.1 Tensile test

For the mechanical tests, notably tensile and flexion, a MTS Alliance RF/200 was used (shown in Figure 2.9). For tensile tests, the specimens were prepared by injection molding according to ASTM D638-10-Type I measuring 190 x 19 x 3.1 mm (see Figure 2.10).

The initial distance between the grips was 115 mm. The tensile modulus, strength, and strain were evaluated at a crosshead speed of 5 mm/min and load cell of 1 kN. At least five tests were used to calculate an average value for each material tested. The measurements were done using an extensometer.



Figure 2.9 MTS Alliance RF/200 w/ tensile mechanical grips

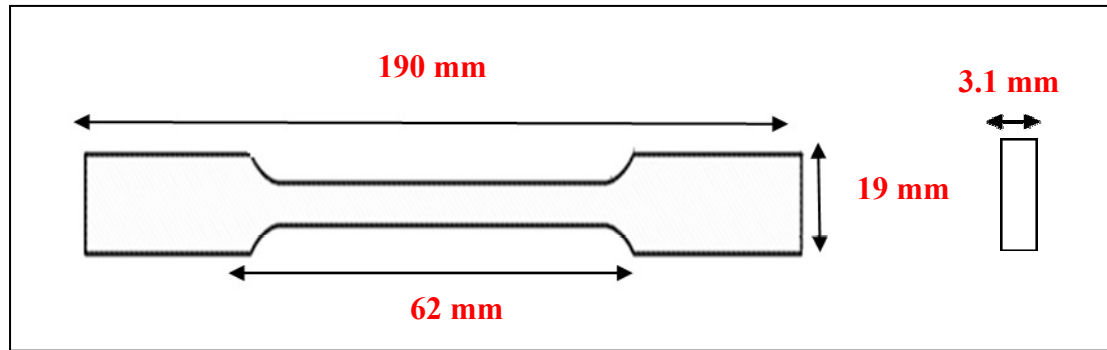


Figure 2.10 Tensile specimen dimensions according to ASTM D638-10-Type I

2.2.3.1.2 Flexure test

A three point bending flexural setup was used to carry out the flexural tests. Specimen dimensions were 127 x 12.7 x 3.1 mm according to the ASTM D790-10. The flexural test was stopped if the specimen deflection reached 5% or if the sample completely broke before the deflection limit. The load cell was 1000 N and the rate of crosshead motion can be calculated by the equations used for L, R and D as follows:

$$R = \frac{ZL^2}{6d} \quad (2.2)$$

Where

R = rate of crosshead motion, mm (in.)/min,

L = support span, mm (in.),

d = depth of beam, mm (in.), and

Z = rate of straining of the outer fiber, mm/mm/min (in./in./min). Z shall be equal to 0.01.

So: $L = 16 \times \text{depth} = 16 \times 3.1 = 49.6 \text{ mm}$

Then: $R = \frac{0.01(49.6)^2}{6 \times 3.1} = 1.32 \text{ mm/min}$

Five specimens were tested with a crosshead speed of 1.3 mm/min and the test was stopped if the specimen deflection reached 5% or if it completely broke before that deflection limit

$$D = \frac{rL^2}{6d} \quad (2.3)$$

Where:

D = midspan deflection, mm (in.),

r = Strain, mm/mm (in. /in.),

L = support span, mm (in.), and

d = depth of beam, mm (in)

$$\text{So: } D = \frac{0.05L^2}{6d} = \frac{0.05(49.6)^2}{6 \times 3.1} = 6.61 \text{ mm}$$

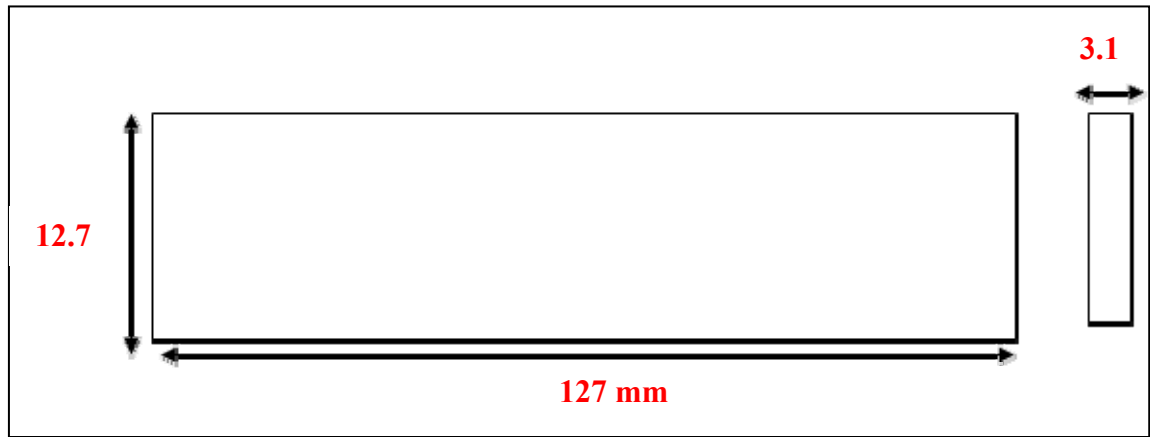


Figure 2.11 Flexural specimen dimensions according to ASTM D790-10

2.2.3.2 Microscopy

Scanning electron microscopy (SEM) Hitachi 3600N SEM operated at 20 kV was used to analyze the microstructure and morphology of the samples obtained by injection molding. Before observation the samples surfaces of composite were cryo-microtomed with a diamond knife at -150°C under nitrogen. Then, it was coated, using the Quorum Q150T, with gold vapor deposition for 120 s and a thickness of 20 nm under vacuum conditions.

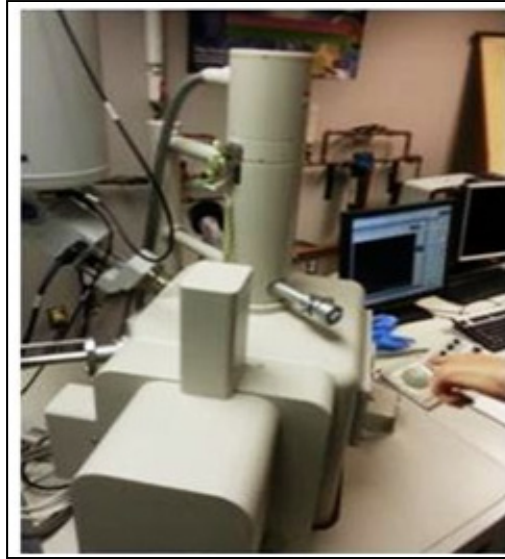


Figure 2.12 Hitachi 3600N SEM

2.2.3.3 Water Absorption uptake

The water absorption of various composites was measured according to ASTM D-570-98. Three specimens for every composite with dimensions of 127 x 12.7 x 3.1 mm, were dried in an oven for 24 h at 50°C and then cooled at room temperature under vacuum. The initial mass for each sample was evaluated and then the specimens were immersed in a container of distilled water maintained at room temperature. To measure the water resistance of different composites, the specimens were removed from water, wiped with paper, weighed the mass gain and then immersed again in water. These steps were repeated for different measurement during 2h, 24h, 1week and 2 weeks. All mass measurement was done using an instrumental balance with a precision of 0.0001 g. The equation used to calculate percent water absorption was as the following:

$$\text{Percent Water Absorption (\%)} = \frac{\text{Wet weight} - \text{Dry weight}}{\text{Dry weight}} \times 100 \quad (2.4)$$

CHAPTER 3

RESULTS AND DISCUSSION

This chapter presents the experimental results. These results are then analyzed and compared with similar works in the literature review.

3.1 HDPE/NCC nanocomposites

3.1.1 Optimization of processing parameters for preparation of HDPE/NCC/ CA1 blends

3.1.1.1 Effect of processing temperature

The compounding process can significantly affect the quality of the HDPE based nanocomposite and the dispersion of NCC in the polymer matrix. One of the purposes of this study was to investigate the effect of compounding conditions on the mechanical properties of HDPE/NCC nanocomposite.

In particular, the processing temperature for melt compounding of nanocomposite based natural nanofillers is a critical parameter. On one hand, at too low temperatures, it is not possible to obtain good composites because diffusion is too slow. On the other hand, a too high processing temperature could result in a thermal degradation and decrease of mechanical properties of fillers (200°C) (E.Jakab, O.Faix et al. 1997, RINGUETTE 2011).

In order to optimize the processing temperature, composites were processed at temperatures ranging from 150°C to 190°C in a 10°C interval. The materials obtained were characterized visually. Also, the curves of torque obtained during processing were analyzed to check for thermal degradation. Table 3.1 presents the physical aspect of the blends obtained and Figure 3.1 the torque curves.

Looking at Table 3.1, it can be seen that when the temperature was raised, the color of the samples changed. The samples became more yellow as the temperature was raised.

According to the results presented in Table 3.1 and Figure 3.1 a temperature of 160°C was chosen for processing the samples. This temperature was selected for the rest of the project.

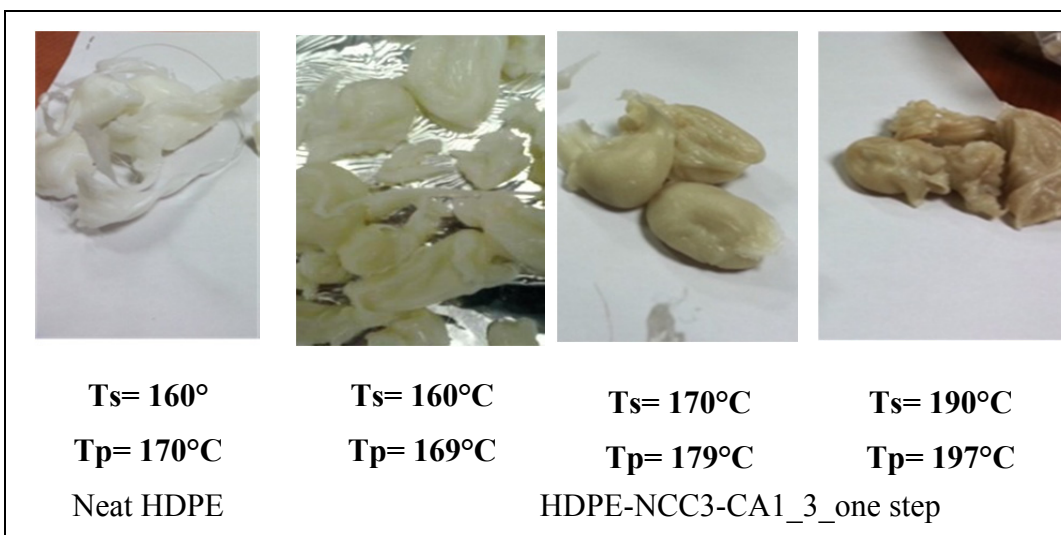


Figure 3.1 Effect of processing temperature on the degradation of HDPE/NCC compounding (mixed balls) where Ts is Setting temperature and Tp is Maximum processing temperature

For more scientific analysis of processing conditions of HDPE nanocomposite, the effect of temperature on melt torque curve was evaluated. Figure 3.1 shows the different curves of torque variation as a function of time for every setting temperature. At the beginning of the compounding, for all processing temperature, the torque of composite was increased rapidly due to the decrease of mixer chamber temperature by adding cold HDPE and compatibilizer. However, after polymer was melted, the melt torque was decreased and leveled off to around 24–35 Nm, depending on the setting temperature, being lower at high temperatures as expected.

When the torque was stabilized (after 4 min of adding HDPE/compatibilizer), the nanocelluloses were added to the mixture. As shown in Figure 3.1., adding nanocellulose, in any case did not seem to have an effect on the torque values proving that the viscosity of the mixture was not changed upon addition of NCC A lot of studies have been reported in the litterature (Panaitescu, Radovici et al. 2011, Sajjadi Jazi, Nasr Esfahany et al. 2012, M. Ceraulo 2014, Mohammed H. Al-Saleha 2013) showing that the incorporation of

nanoparticles in polymer matrix with good dispersion increase their viscosity and torque due to interactions and friction that can occur between the polymer chains and nanoparticles limiting their movement. However, this variation becomes negligible in the case of small amount of filler (Sahoo, Maiti et al. 2007, Panaitescu, Radovici et al. 2011, M. Ceraulo 2014, Mohammed H. Al-Saleha 2013).

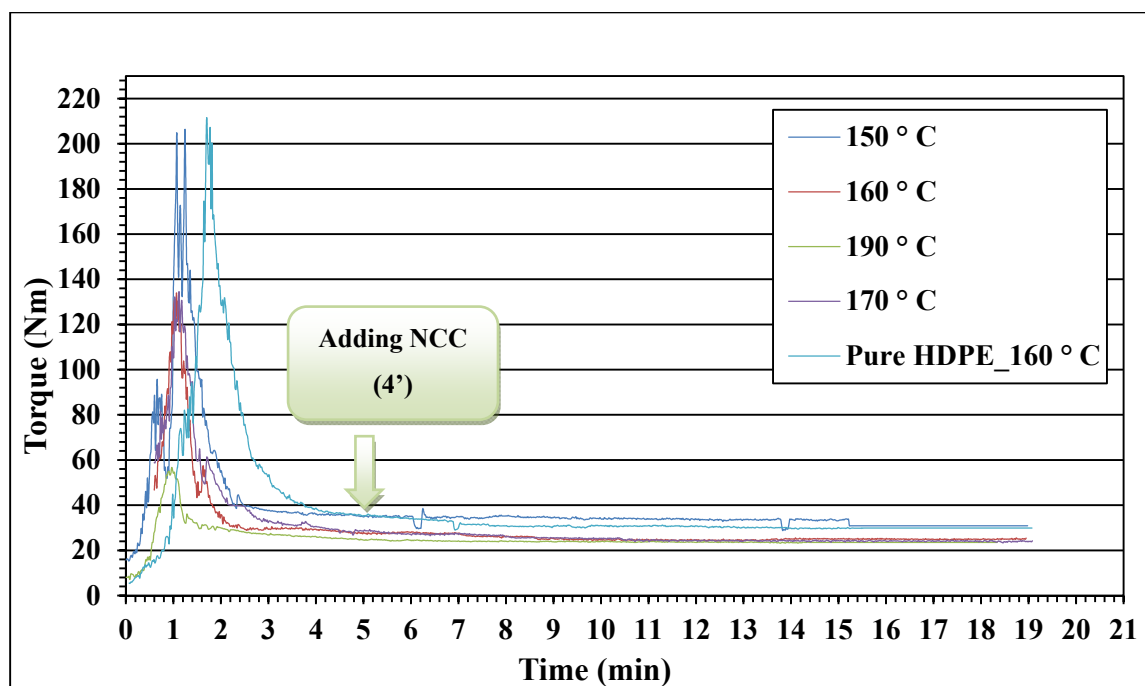


Figure 3.2 Compounding characterization of the melt torque of the pure HDPE and HDPE-NCC3-CA1_3 at different processing temperatures

In the case of the present work, adding 3 % NCC into HDPE matrix did not result in a significant effect on torque values. This result indicates a poor dispersion of NCC or even that the amount of added NCC was very low to create a change of torque values. Figure 3.2 presents the influence of % of NCC on the torque curves. Two different NCC content were evaluated 3 and 10 wt.%, It can be seen that upon addition of 10 wt.% NCC the torque increased indicating that 3 wt.% NCC did not result in an increase of torque due to the low content of NCC added.

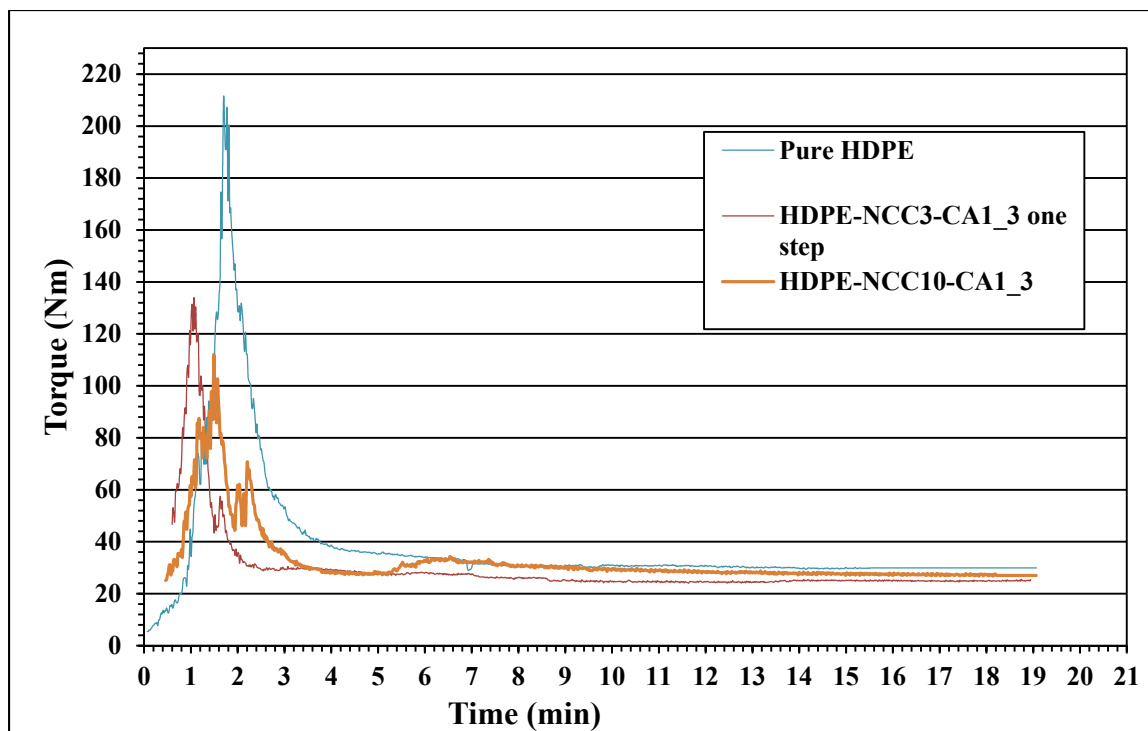


Figure 3.3 Effect of NCC loading on melt torque of HDPE nanocomposite

3.1.1.2 Comparison of one-step (direct mixing) and two-step (masterbatch) procedures.

The compounding of HDPE/NCC/CA1 was carried using two different methods as reported in the experimental procedures: 1) in one step method, all compounding ingredients were directly mixed, together, using an internal mixer (as has been previously described in first 2.2.1) in two step processes, a masterbatch of NCC diluted in compatibilizing agent (CA1) was obtained and then mixed to HDPE. For this second method, the masterbatch (50% NCC/50% CA1) was obtained using a small internal mixer (30 cm³) at a temperature of 140°C and rotor speed 50 rpm for 10 min under nitrogen atmosphere (shown in Figure 3.3). The aim of using masterbatch was to improve the compatibility and dispersion of NCC within HDPE matrix by chemical modification with maleic anhydride grafted on CA1. At the same composition, the torque curves, presented in Figure 3.4, show that there is no differences between similar samples prepared by the two methods (the same result was

obtained by Denis Mihaela Panaitescu (Panaitescu, Radovici et al. 2011) with $\text{TiO}_2/\text{LLDPE}$). This result confirms that upon addition of 3% NCC, there is no effect of the preparation method chosen on the value of torque. However, their effect on the dispersion of NCC will be discussed later through flexural tests and SEM observations.

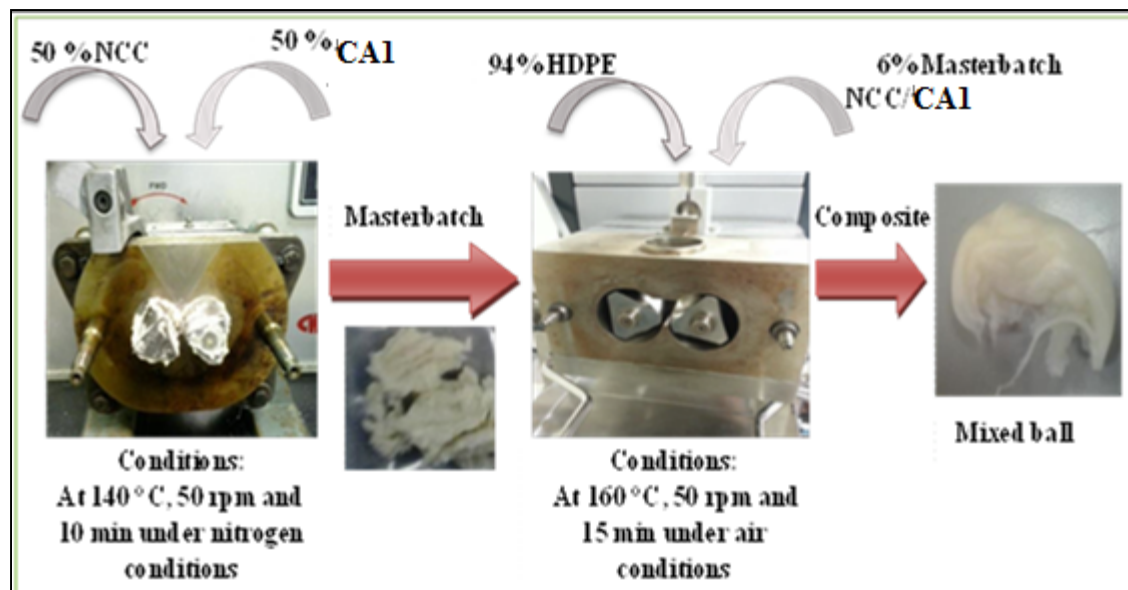


Figure 3.4 Two steps melt compounding of HDPE/NCC/ CA1 in the internal mixer

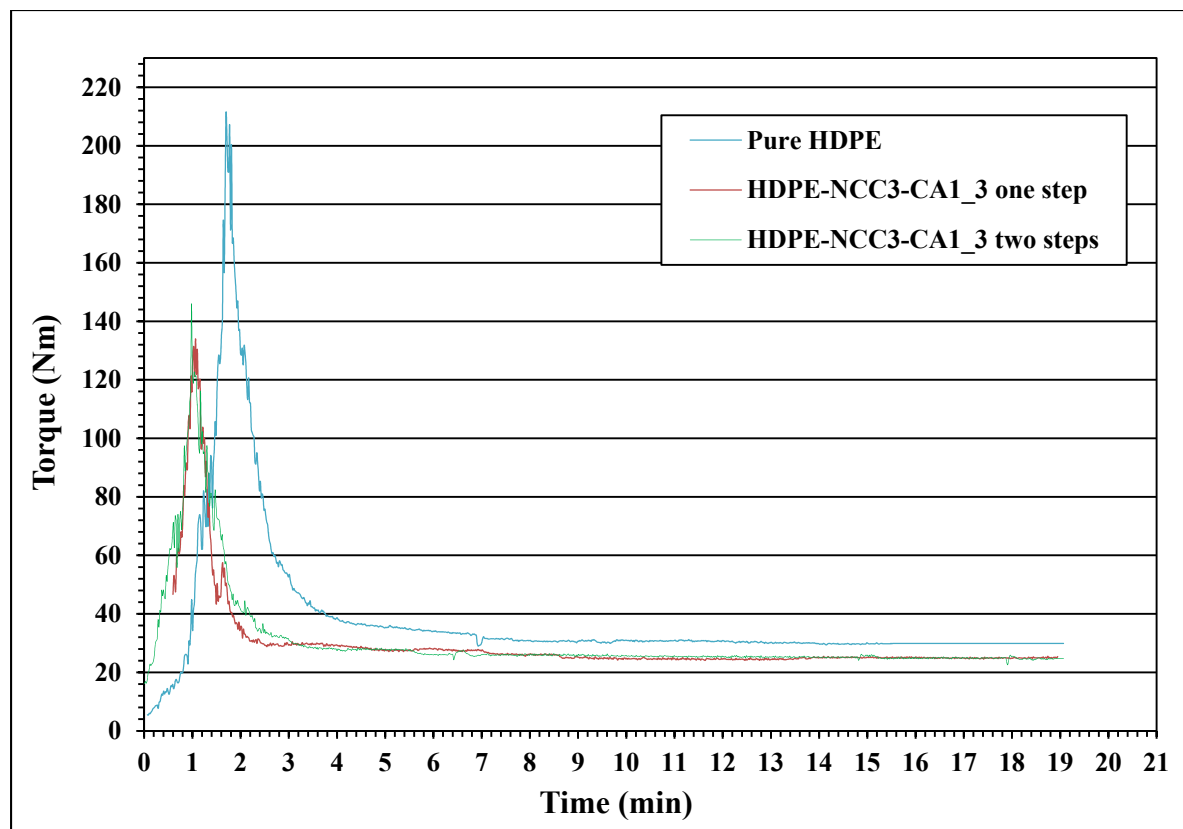


Figure 3.5 Effect of processing conditions, one step and two steps compounding, on melt torque of HDPE nanocomposite

3.1.1.3 Injection molding processing temperature optimization of the HDPE/NCC

Knowing that NCC degradation has a negative effect on the mechanical properties of nanocomposites, the optimization of processing temperature for each compounding steps must be done. As it was done in the case of mixer chamber temperature, several injection processing temperatures were tested (barrel temperature) to find the best conditions to avoid the degradation of NCC (see in Table 3.2). Our analysis is always based only on the visual appearance of the samples. Table 3.2 presents the physical aspect of the injected samples. It can be seen from the pictures presented in Table 3.2, the color of samples range from clear yellow to deep yellow with increasing the injection temperature. This variation can be an indication of increased degradation of NCC. Therefore, the best temperature to be chosen for

our project will be 180°C. At this temperature, the degradation is insignificant and the color change is due mainly to the compounding mixer.

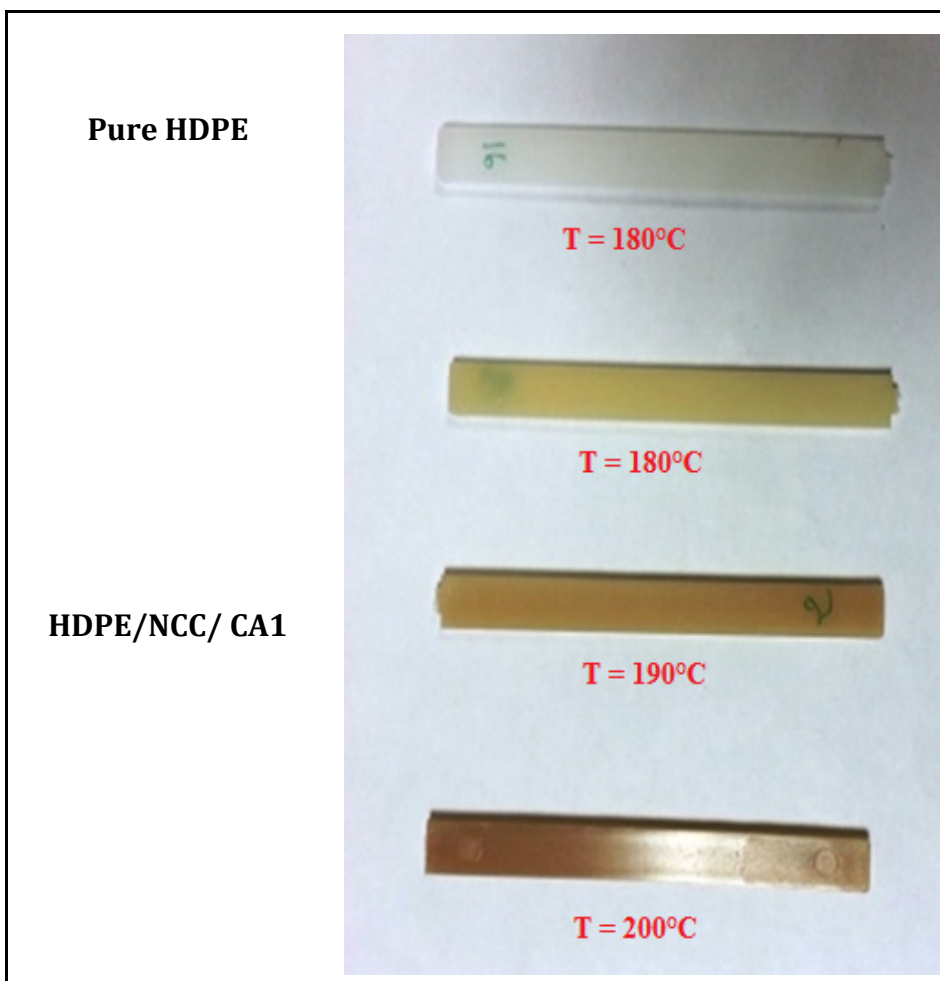


Figure 3.6 Effect of injection molding processing temperature on the HDPE/NCC nanocomposite aspect (degradation of NCC)

3.1.2 Flexural properties

Table 3.3 presents the results of flexural modulus and strength measurements of different nanocomposites HDPE with the addition of NCC and the presence of compatibilizing agent (CA1 and CA2).

Table 3.1 Flexural test results for HDPE/NCC/compatibizer composites

Code/composition	Peak Load (N)	Ult. flexural strength (MPa)	Flexural modulus (MPa)	Strain (mm/m m)
HDPE	31.15 +/-0.12	19.03 +/- 0.08	1074 +/- 43	5%
HDPE-CA1_3	29.73+/-0.05	18.44 +/- 0.05	948 +/- 25	5%
HDPE-CA2_3	30.18+/-0.18	18.73 +/- 0.12	983 +/- 25	5%
HDPE-NCC10	38.62 +/-1.41	23.78 +/- 0.88	1239 +/- 40	5%
HDPE-NCC10-CA1_1	37.28 +/-0.06	23.24 +/- 0.05	1229 +/- 30	5%
HDPE-NCC10-CA2_1	38.61 +/-0.16	24.06 +/- 0,09	1322 +/- 37	5%
HDPE-NCC10-CA1_3	37.63 +/-0.16	23.16 +/- 0.1	1315 +/- 42	5%
HDPE-NCC10-CA2_3	38.23 +/-0.10	23.83 +/- 0.05	1305 +/- 49	5%
HDPE-NCC3-CA1_3 one step	31.71 +/- 0.12	19.6+/-0.10	1146 +/- 31	5%
HDPE-NCC3-CA1_3_two step	33.83 +/-0,14	20.8 +/- 0,08	1183 +/- 29	5%
HDPE-NCC10-CA1_10	35.36 +/-0,23	21.77 +/- 0.13	1217 +/- 22	5%

The comparison of flexural results of stress-strain curves between the different nanocomposites is shown Figure 3.5. It can be seen from Figure 3.5, that the flexural modulus and strength increased upon increasing NCC content and upon addition of either compatibilizing agent. The best results of flexural tests were obtained upon addition of 10% of NCC and 1% of CA2 (HDPE-NCC10-CA2_1). Compared to pure HDPE, the flexural strength was increased by more than 26 % and the flexural modulus by more than 23 %. However, there is no significant difference between this result and the results obtained for HDPE-NCC10 (without compatibilizer) and HDPE-NCC10-CA1_3 (with 3% CA2). To

identify the best compositions of composite with optimized mechanical properties the effect of each single parameter alone was evaluated separately.

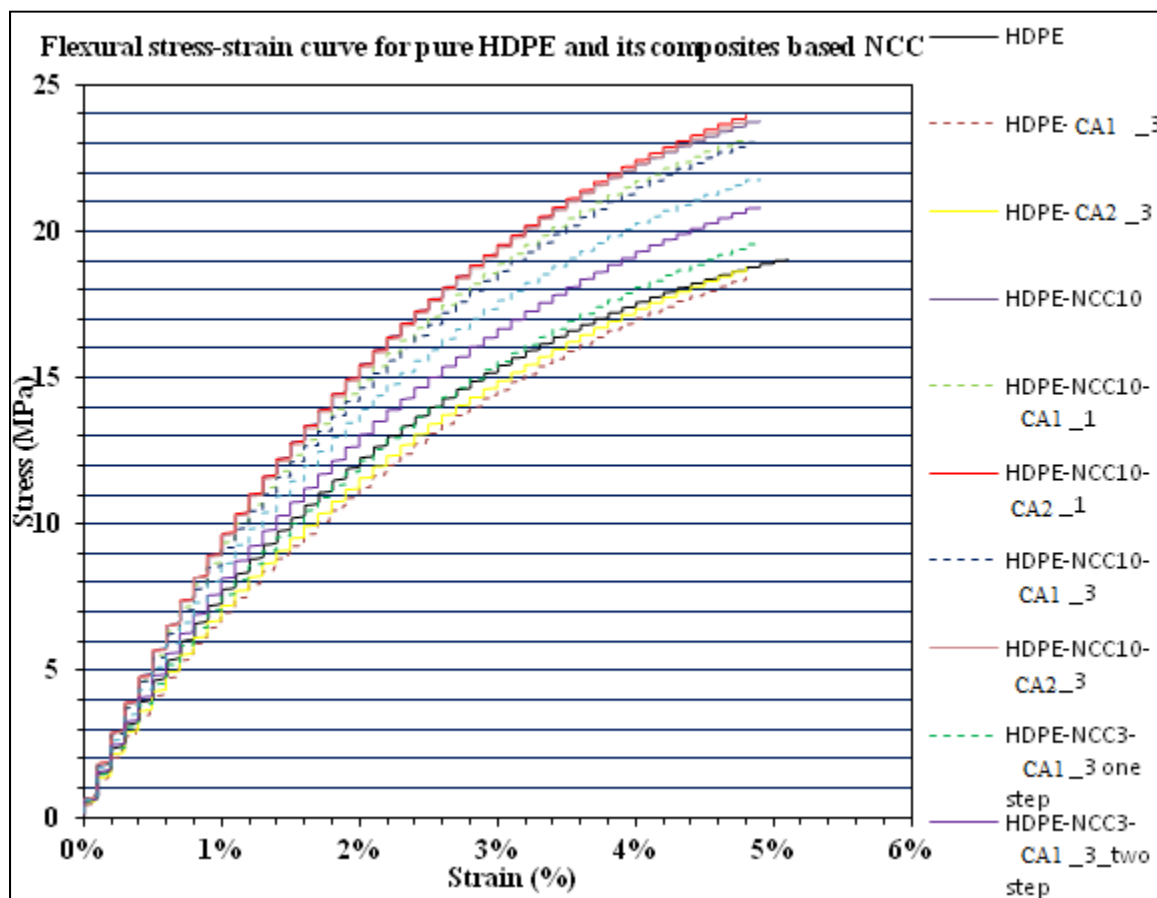


Figure 3.7 Flexural stress-strain curve for pure HDPE and its composites based NCC

3.1.2.1 Effect of processing methods

The compounding of nanocomposite with masterbatch is mainly used to improve the compatibility between the fillers and the polymer matrix. Indeed, this additional step can be used as a surface chemical modification of the NCC to improve their dispersion into the polymer and help to have more evenly distributed compatibilizer at the interface between the NCC and polymer. In this step we will try to investigate the effect of compounding procedure on the flexural strength and flexural modulus of HDPE/NCC/CA1 composite. As seen in

Figure 3.6, it is clear that the two-step process generates better flexural strength and flexural modulus than processing in a single step. However, upon addition of 3 % NCC, the use of masterbatch did not have a very significant effect in comparison with the pure polymer or one step process. So, this result shows that the use of masterbatch process does not improve the dispersion of NCC. Moreover this additional step could be detrimental to the quality of the material. A verification of the efficacy of CA1 to disperse NCC in HDPE was examined by SEM observations of microtomed flexural samples surfaces (look at Figure 3.11). Big agglomerations of NCC are observed in both cases of compounding techniques which indicate a poor dispersion.

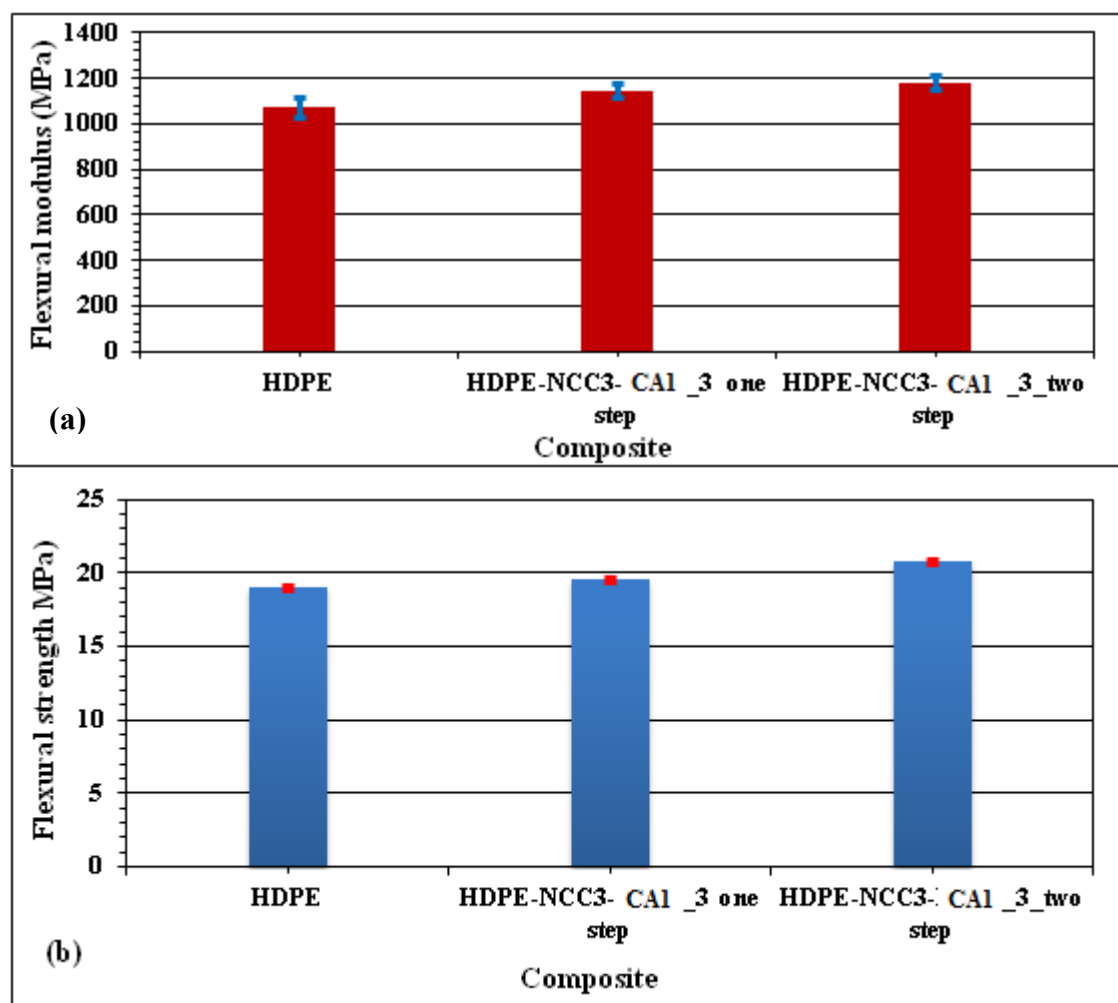


Figure 3.8 Effect of mixing method: one step and two step mixing on the (a) flexural modulus and (b) strength of HDPE composites at 3% NCC and 3% CA1

3.1.2.2 Effect of NCC content

Figure 3.7 presents the effect of NCC content on the flexural properties. It can be seen that both, the flexural strength and modulus increased upon increase of NCC content. At a load of 3% of NCC, the improvement of flexural properties is not significant but with increasing the NCC content to 10% the flexural modulus and flexural strength increased by 38.7% and 25.6%, respectively, compared to HDPE/CA1. Similar results with different reinforced materials were reported in previous researches (Devi, Shashidhara et al. 2010, Niranjana Prabhu and Demappa 2014, Tong, Royan et al. 2014, Bravo, Toubal et al. 2015).

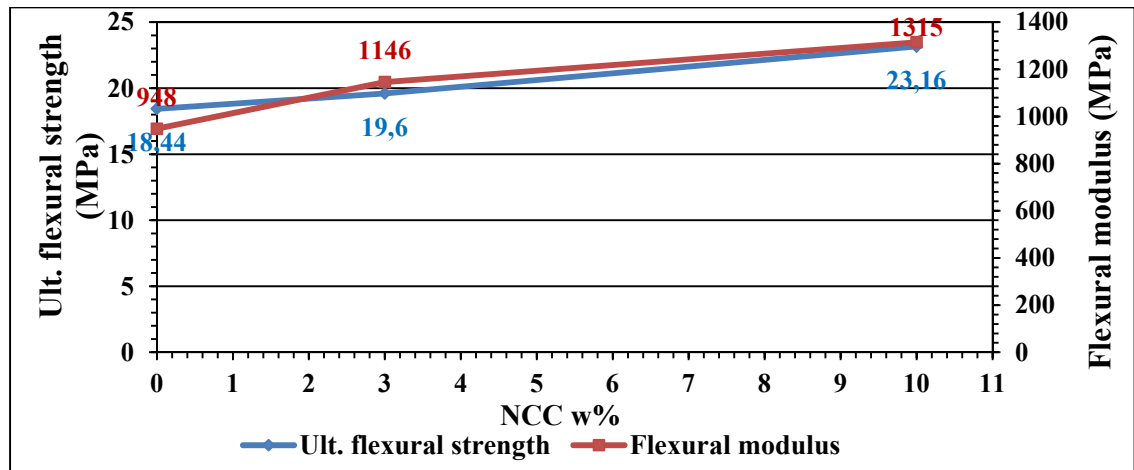


Figure 3.9 Effect of NCC content (0%;3% and 10%) on flexural modulus and strength of HDP/NCC/CA1 composite in the presence of 3% CA1

3.1.2.3 Effect of type and concentration of compatibilizing agent

Two types of compatibilizing agent, CA1 and CA2, have been used to improve the adhesion between NCC and HDPE. Figures 3.8 and 3.9 show a comparison of flexural strength and modulus between the composites based on compatibilized and uncompatibilized NCC as well as the effect of compatibilizer type and concentration. Adding compatibilizing agent to HDPE resulted in a decrease of the mechanical properties of the pure resins most likely due

to the poor mechanical properties of MAgPE (see Figure 3.8). This decrease is more significant in the case of CA1 because its viscosity is lower than CA2 ($\eta_{CA1} = 1/2 \eta_{CA2}$).

In the case of composite HDPE / NCC, it is clearly observed in Figure 4.8 that adding compatibilizing agent results in an improvement of the flexural strength and modulus of nanocomposite for both types of compatibilizer. This improvement was optimal in the case of CA2 with 1% concentration. Indeed, flexural strength was increased by 26 % and the flexural modulus by 23 % in comparison to pure HDPE. However, increasing the concentration of compatibilizing agent from 1% to 3% then 10% led to a slight decrease of mechanical propriety. This can be explained by the decrease of HDPE properties with adding compatibilizer. Also, it is well observed that the CA2 shows better results than CA1.

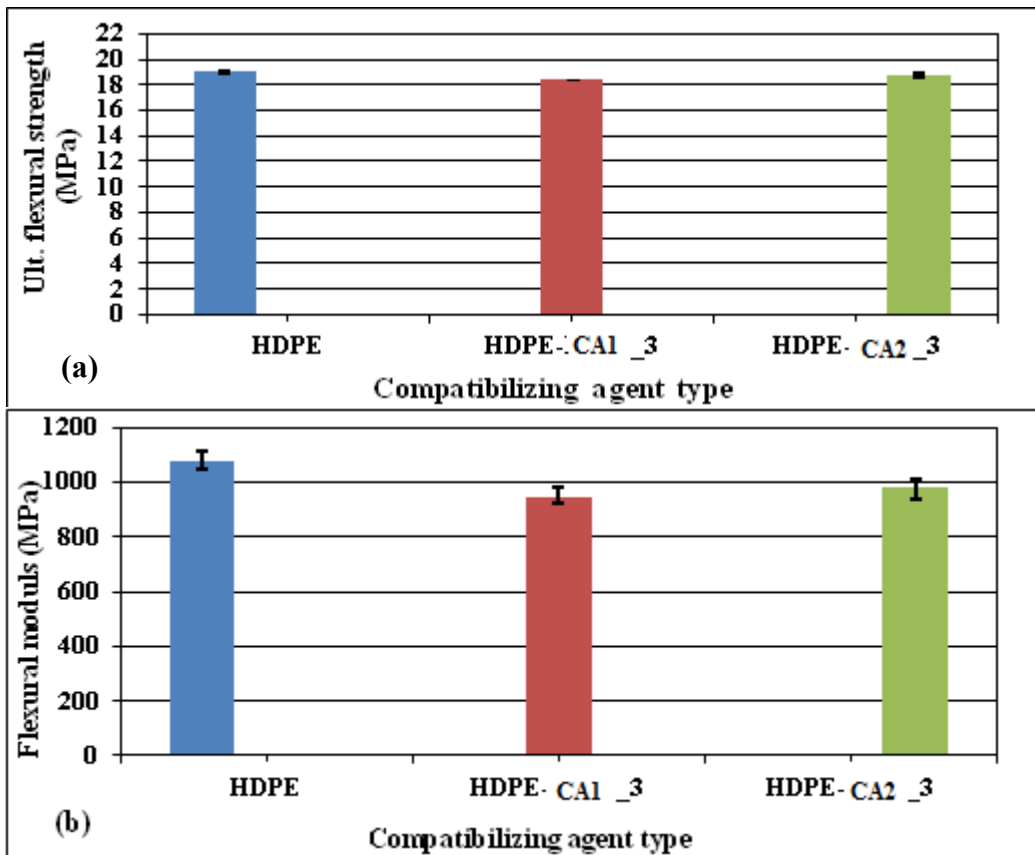


Figure 3.10 Effect of compatibilizing agent type on the (a) flexural strength and (b) modulus of HDPE

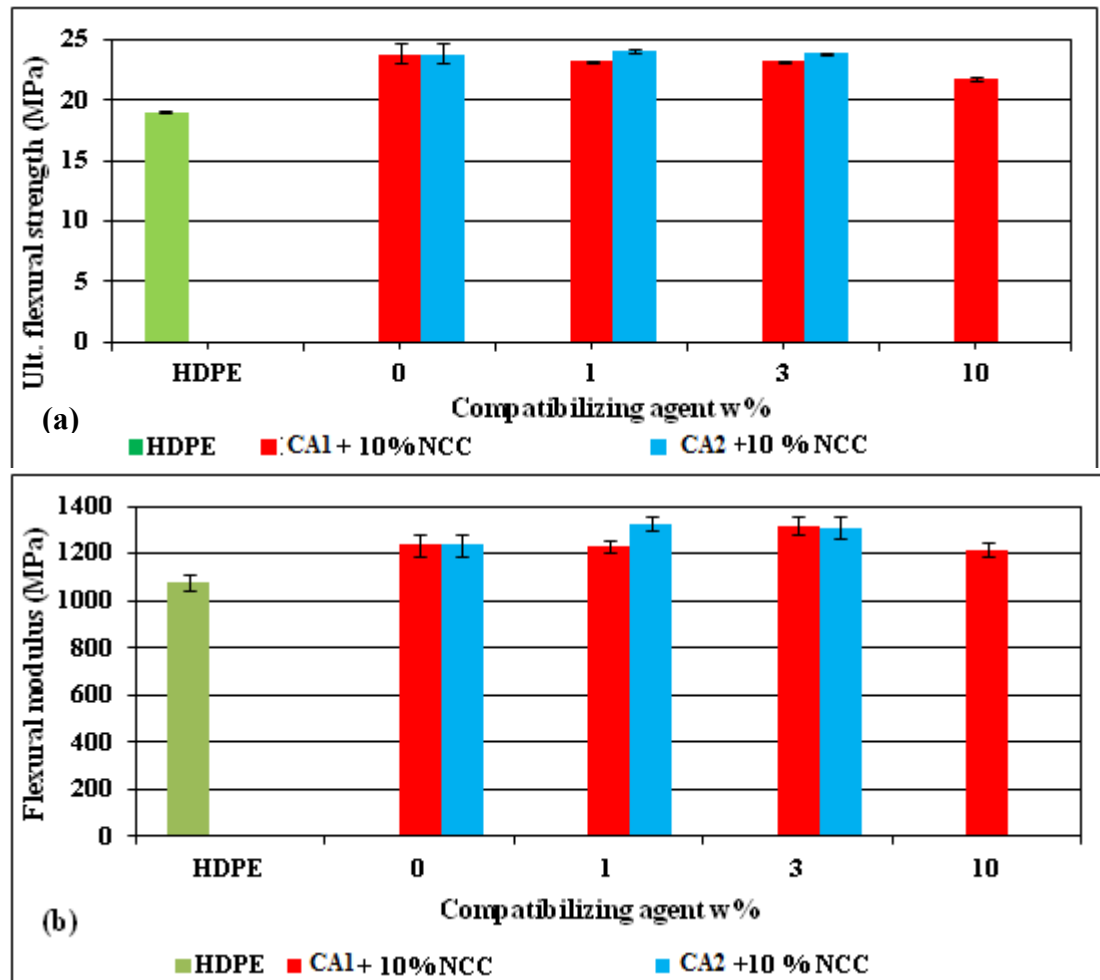


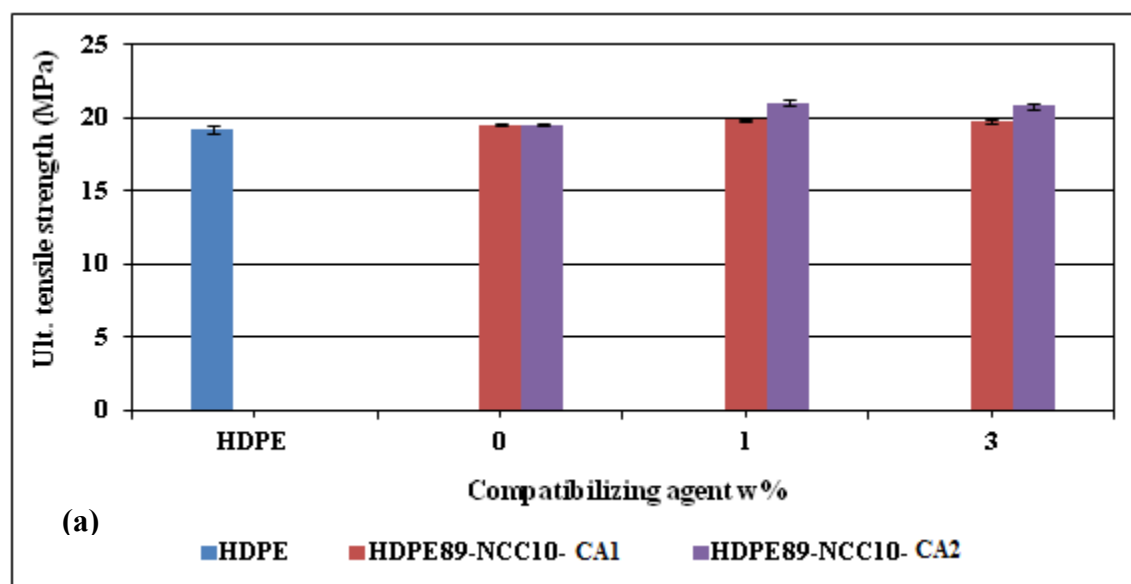
Figure 3.11 Effect of compatibilizing agent type and loading on the (a) flexural strength and (b) modulus of HDPE/NCC composite at 10% of NCC content

3.1.3 Tensile properties

Tensile properties of the samples that presented the best flexural properties were evaluated using the MTS Alliance RF/200 according to ASTM D638. The results for ultimate tensile strength; Young modulus and elongation at break are presented in Table 3.4 and Figure 3.10.

Table 3.2 Tensile test results for HDPE/NCC/compatibilizer composites

Code/composition	Ult. tensile strength (MPa)	Tensile modulus (MPa)	Strain at break (mm/mm)
HDPE	19.22 +/- 0.26	816 +/- 63	>400%
HDPE-NCC10	19.53 +/- 0.12	766 +/- 21	>400%
HDPE-NCC10-CA1_1	19.85 +/- 0.06	1035 +/- 16	>400%
HDPE-NCC10-CA2_1	21 +/- 0,22	1164 +/- 63	>400%
HDPE-NCC10-CA1_3	19.75 +/- 0.13	1107 +/- 31	>400%
HDPE-NCC10-CA2_3	20.80 +/- 0.14	1179 +/- 52	>400%



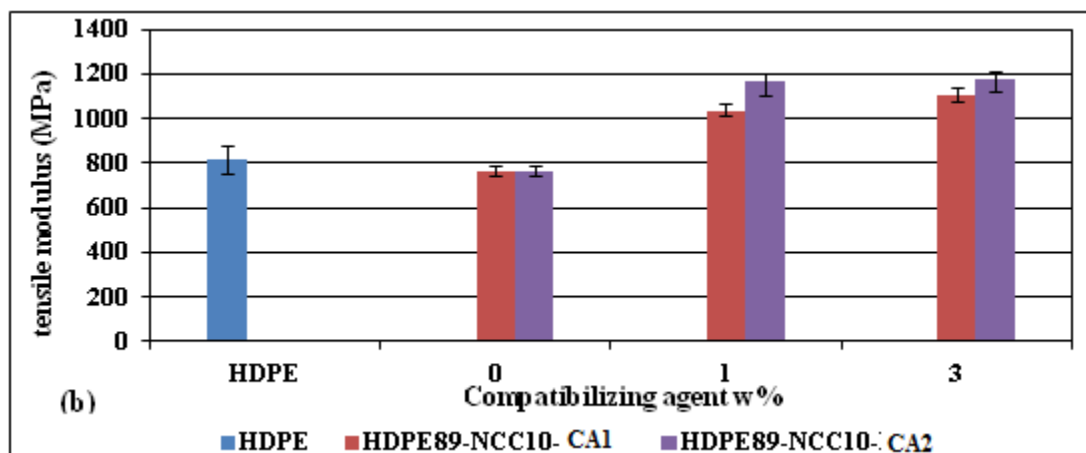
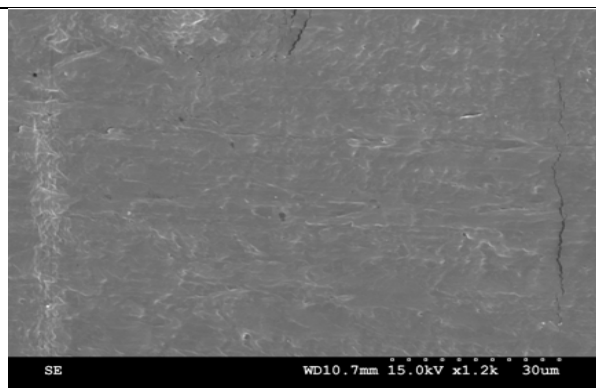


Figure 3.12 Effect of compatibilizing agent type and loading on the (a) tensile strength and (b) modulus of HDPE/NCC composite at 10% of NCC content

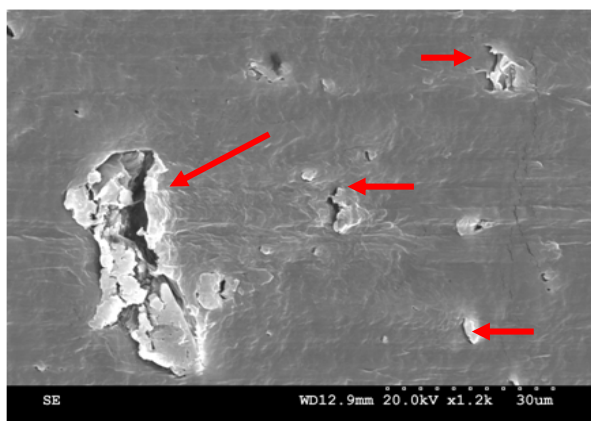
Figure 3.10 shows that adding 10% NCC in HDPE nanocomposites has no effect on ultimate tensile strength but that a reduction of the modulus was observed. This result can be explained by the agglomeration of NCC which causes an insufficient stress transfer between NCC and HDPE matrix. To improve the dispersion of NCC as well as tensile properties of HDPE/NCC nanocomposites, we tested the effect of two types of compatibilizer agents. It can be seen from the results presented Table 3.4 and Figure 3.10 that, the tensile modulus shows an improvement of approximately 44% compared to neat polymer by addition of 1% CA2. However, a slighter increase was observed for ultimate tensile strength. It can also be seen from the results presented Table 3.4 and Figure 3.10 that the addition of CA2 resulted in better results and that the optimal concentration was 1wt%. In fact, increasing the compatibiliser concentration from 1% to 3% did not improve the tensile properties of nanocomposites. This is can be due to the low mechanical properties of compatibilizer compared to neat HDPE.

3.1.4 Scanning electron microscopy analysis

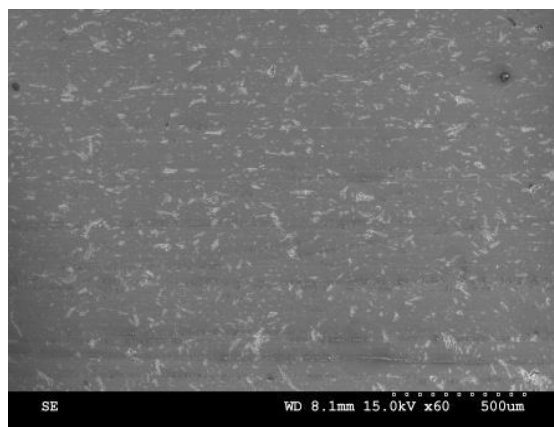
It is well known that, the morphology of polymer composites and the dispersion of nanoparticles is a very important characteristic because they explain the results obtained for mechanical properties. Figure 3.11 shows the images of a microtomed surface of metalized specimens obtained using SEM.



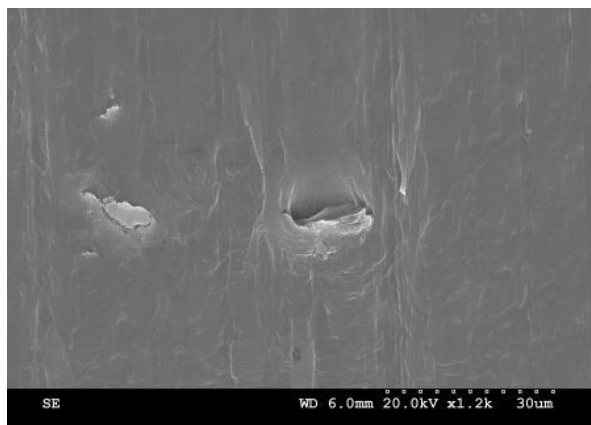
HDPE (x1.2 K)



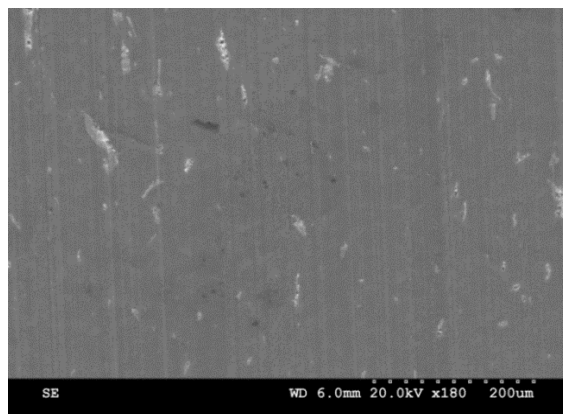
HDPE-NCC10 (x1.2K)



HDPE-NCC10 (x60)



HDPE-NCC3-CA1_3 one step (x1.2K)



HDPE-NCC3-CA1_3 one step (x180)

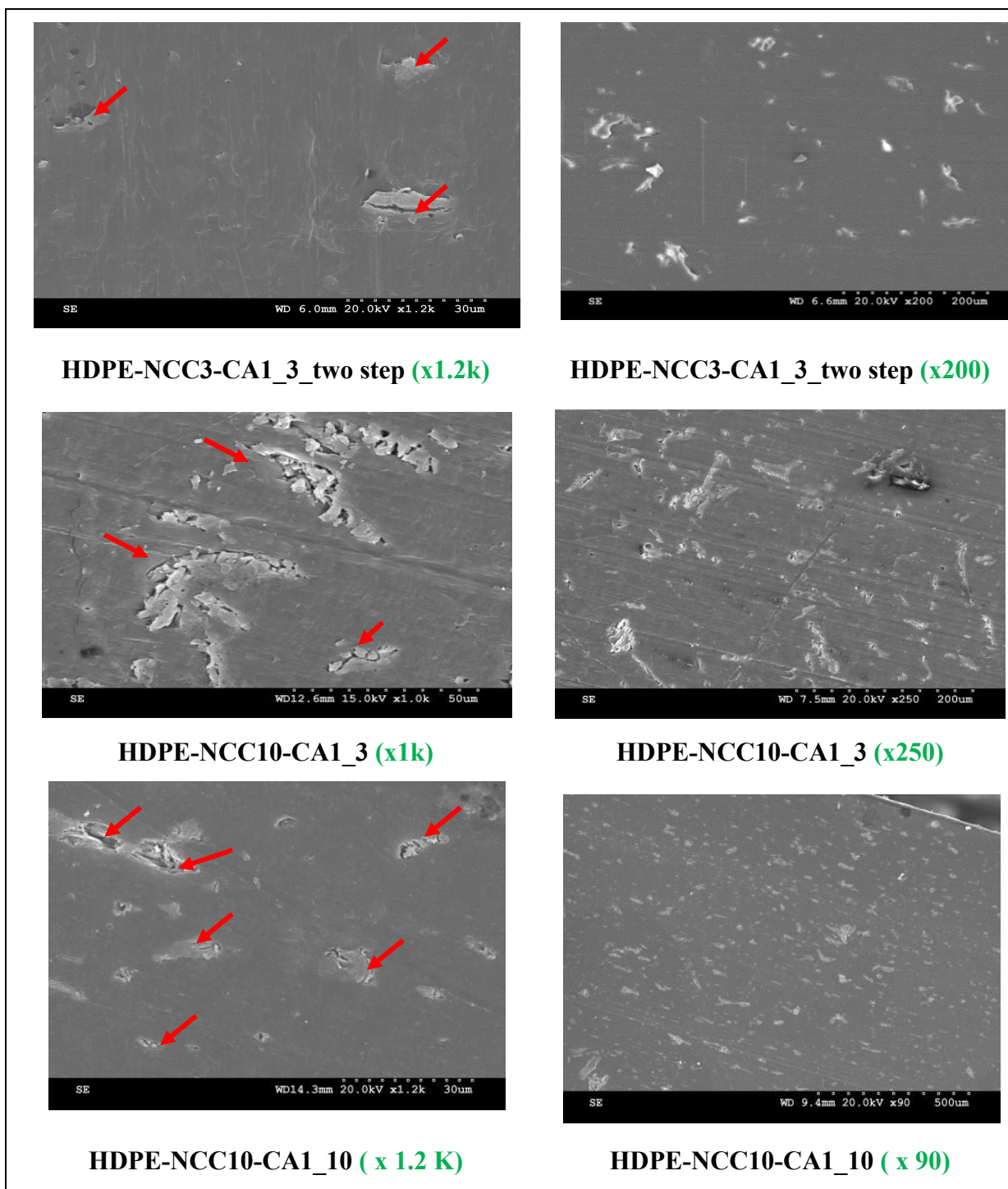


Figure 3.13 SEM images of microtomed surfaces for composites at different magnifications: pure HDPE, HDPE-NCC10, HDPE-NCC3-CA1_3 one step, HDPE-NCC3-CA1_3_two step, HDPE-NCC10-CA1_3 and HDPE-NCC10-CA1_10 (red arrows show the NCC agglomerations)

It can be seen that big agglomerates of NCC were formed particularly when 10 % NCC was added to the blend. This result shows that the dispersion of NCC was poor. The results also seem to indicate the addition of CA1 did not seem to have a significant effect to improve the dispersion. This may be due to the low concentration of compatibilizer which was insufficient to cover the large surface area of NCC. However, the deformation observed on the surface of HDPE where they have the agglomerations of NCC may indicate that the adhesion between NCC and HDPE was good and this deformation was caused by the shearing forces during the cutting of the sample with the diamond knife. Also, at high magnification images we can see that the distribution of NCC was very good. These two last observations can prove that the compatibility of NCC with HDPE was better but remains insufficient to have a good dispersion because of a high surface area of NCC and its tendency to agglomerate. For this purpose, in order to improve the dispersion we tried subsequently to use another technique to incorporate NCC in polymer matrix (aqueous NCC suspensions).

3.1.5 Effect of NCC dispersion technique: water suspension and dry mixing

As seen in the previous section, HDPE / NCC composites with or without compatibilizer presented a poor dispersion. For this reason, we tried to use another technique to improve the dispersion of NCC. This technique consisted of dispersing NCC in water before feeding into the polymer matrix. In this step, the samples were prepared using a co-rotating twin-screws micro- extruder to avoid the wasting of materials (see Figure 3.12). A sample of 4g was fed in the extruder at 170°C and a screw speed was 100 rpm to have a torque value of 94 Nm. The time of mixing was fixed to 13 min to approach mixer value without degradation NCC. For the first method (dry mixing), the HDPE and compatibilizer were fed in the extruder. Further the NCC was added to the HDPE/compatibilizer mixture when the polymer was melted (the torque is stabilized). The samples obtained were in the form of fiber which can be characterized later by SEM. The second technique was preparing an aqueous suspension of NCC to have good dispersion then the suspension was fed very slowly in the melted polymer. Figure 3.13 presents the different stages of preparation of the composites HDPE-NCC10 and HDPE-NCC10-CA2_3 using the two methods of dispersion. The

comparison between the two techniques will be based on SEM observation shown in Figure 3.14.

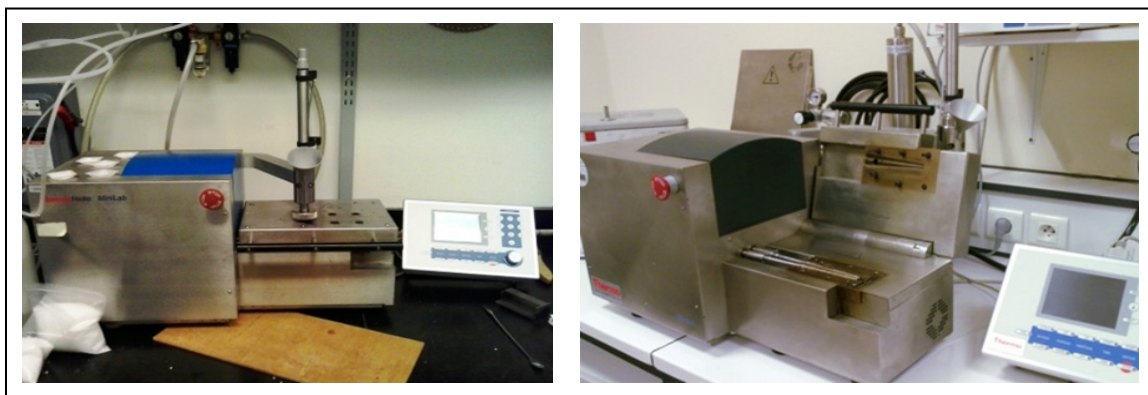


Figure 3.14 Co-rotating twin-screws micro-extruder

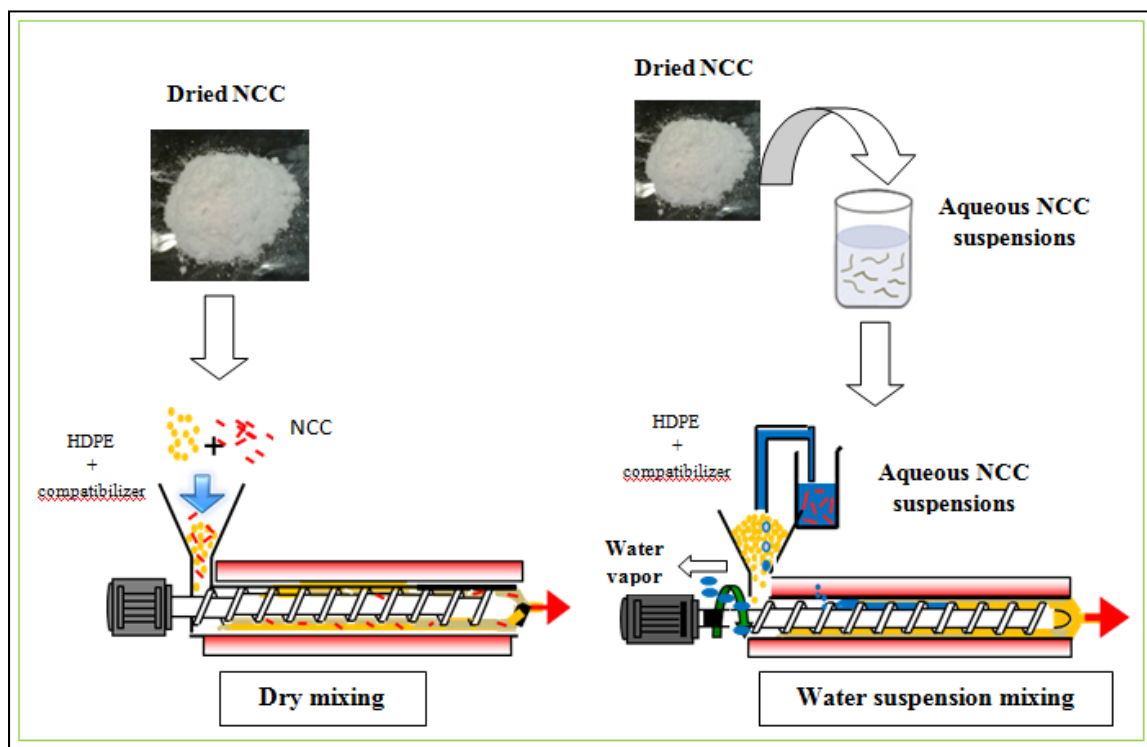


Figure 3.15 Schematic representation of the two techniques, dry mixing (dried NCC) and water suspension mixing (Aqueous NCC suspensions), used for preparation of HDPE/NCC/CA2 composite by micro extruder

It can be seen from the results presented Figure 3.14 that the use of the microextruder did not result in a better NCC dispersion unless a water suspension of NCC was used. These results are promising and further tests could be carried out to test this method on a larger scale.

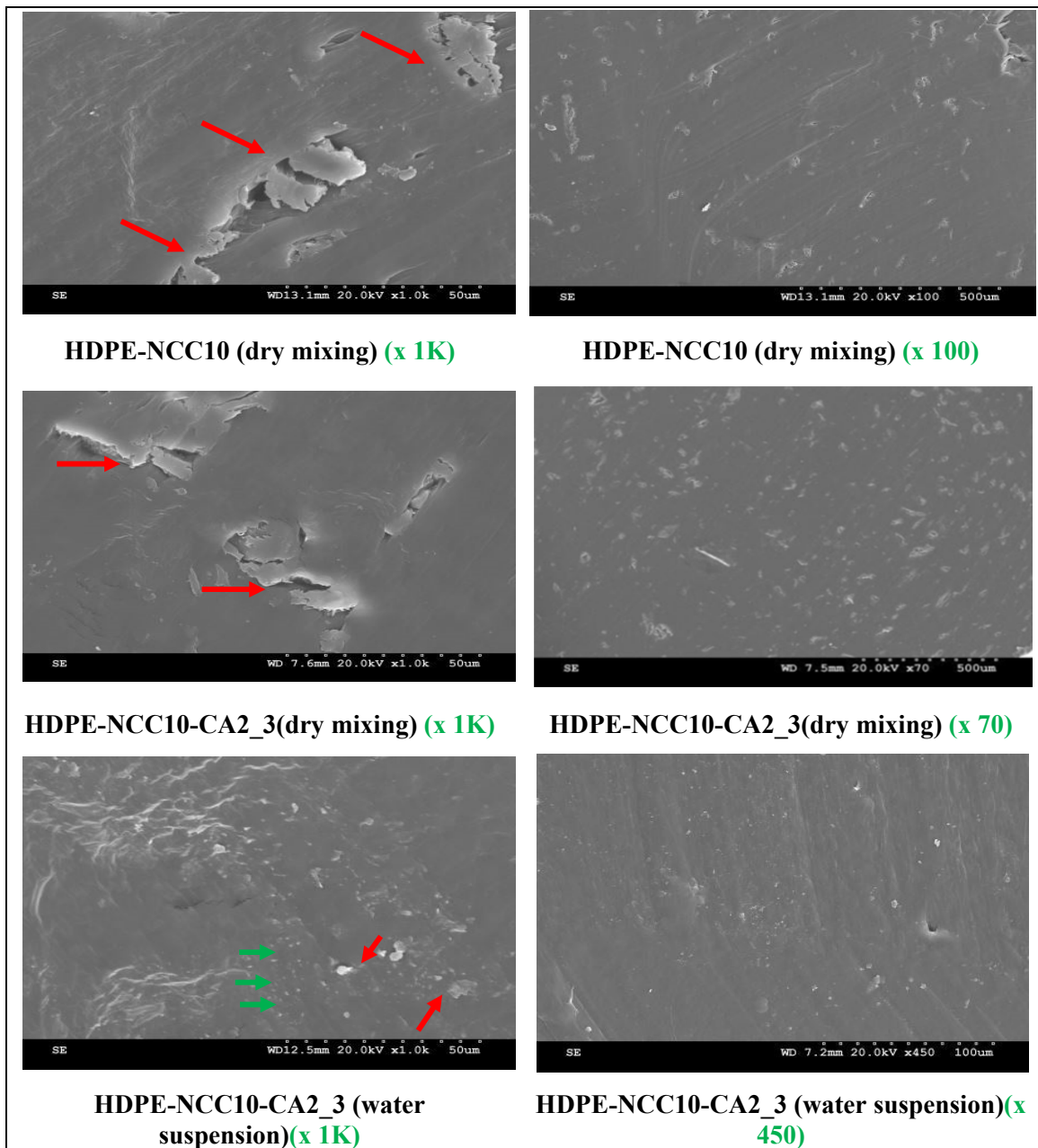


Figure 3.16 SEM images of fracture surfaces for composites at different magnifications: HDPE-NCC10 and, HDPE-NCC10-CA2_3 with two different techniques of mixing (red arrows show the NCC agglomerations and green arrows the good NCC dispersion)

3.1.6 Water Absorption uptake

The water absorption curves of HDPE/NCC nanocomposites are shown in Figure 3.15. The water absorption of various composites increase with increasing of immersion time in water. As a general trend, the water absorption of nanocomposite increase with increasing nanoparticles content from 0% to 10%. The maximum weight gain was obtained with 10% NCC with 0.46% compared to initial mass. When a 3% of compatibilizer agent was added the moisture absorption resistance of HDPE/NCC10 % nanocomposite was improved and the water uptake was reduced to 0.35%. This result is mainly due to the improvement of nanoparticles dispersion. Indeed, a good interfacial adhesion can reduce interactions between hydroxyls groups in the surface of nanoparticles and water, as well as embedding of fibers by polymer. Two processing conditions of HDPE/NCC compounding (direct mixing and two step mixing) was also tested, the results showed that prior mixing of NCC with compatibilizer agent can increase the water absorption resistance of nanocomposite by increasing chemical interactions between NCC and compatibilizer.

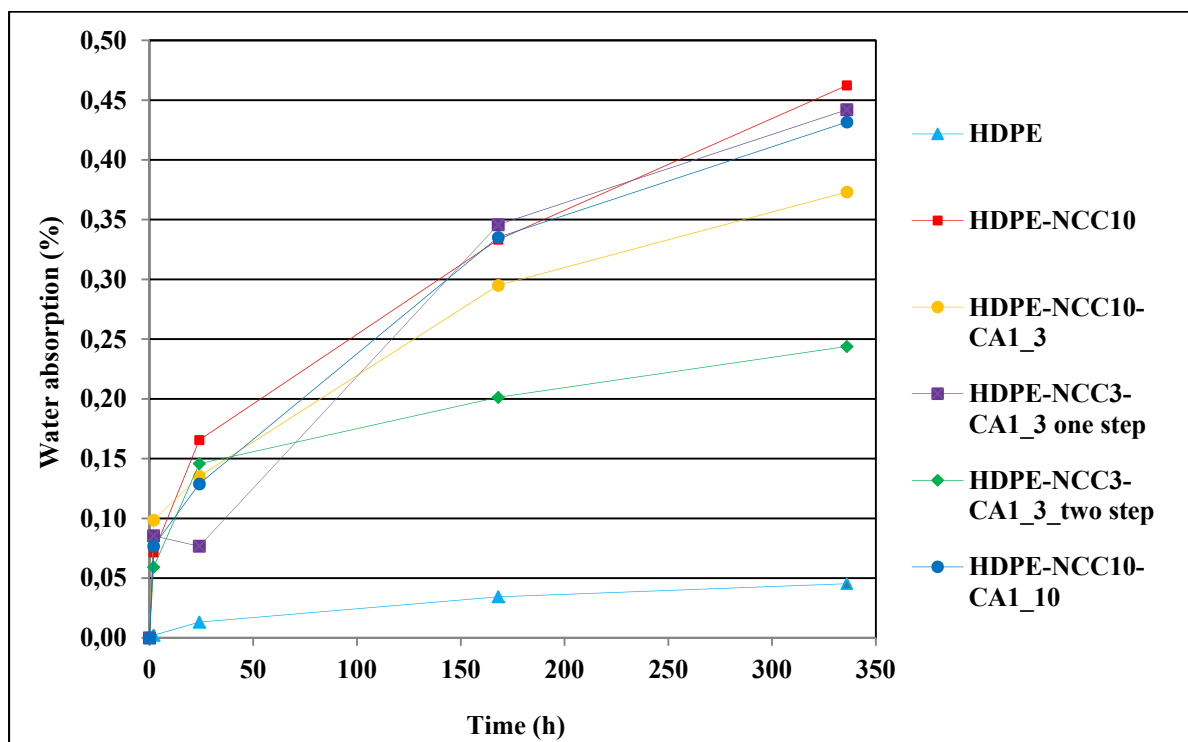


Figure 3.17 Water absorption of different nanocomposites HDPE/NCC

3.2 Hybrid nanocomposites

In the previous section we have studied the mechanical properties and moisture resistance of HDPE/NCC nanocomposites. The effect of nanoparticles content, surface modification with two types of compatibilizer agent and processing condition in internal mixer was also examined to have a good dispersion of NCC on HDPE nanocomposites. In the present section, we tried to compare the mechanical and physical properties of the best condition for HDPE/NCC to some conventional composites based wood flour and sisal, and also to see the effect of adding NCC as a second filler on wood flour composite to have hybrid nanocomposites.

3.2.1 Mechanical properties

Figure 3.16 and Figure 3.17 show the results obtained for tensile and flexural tests of various composites using different fibers as fillers (wood flour, sisal and NCC). The flexural modulus and flexural strength were increased by 105 % and 106% respectively with addition of 30% wood flour and 3% of CA2. This result is much higher than the one obtained for the HDPE/NCC nanocomposite. This can be due to the agglomeration of NCC but also to have a good comparison the same content of filler should be studied using 10 % of wood flour for example.

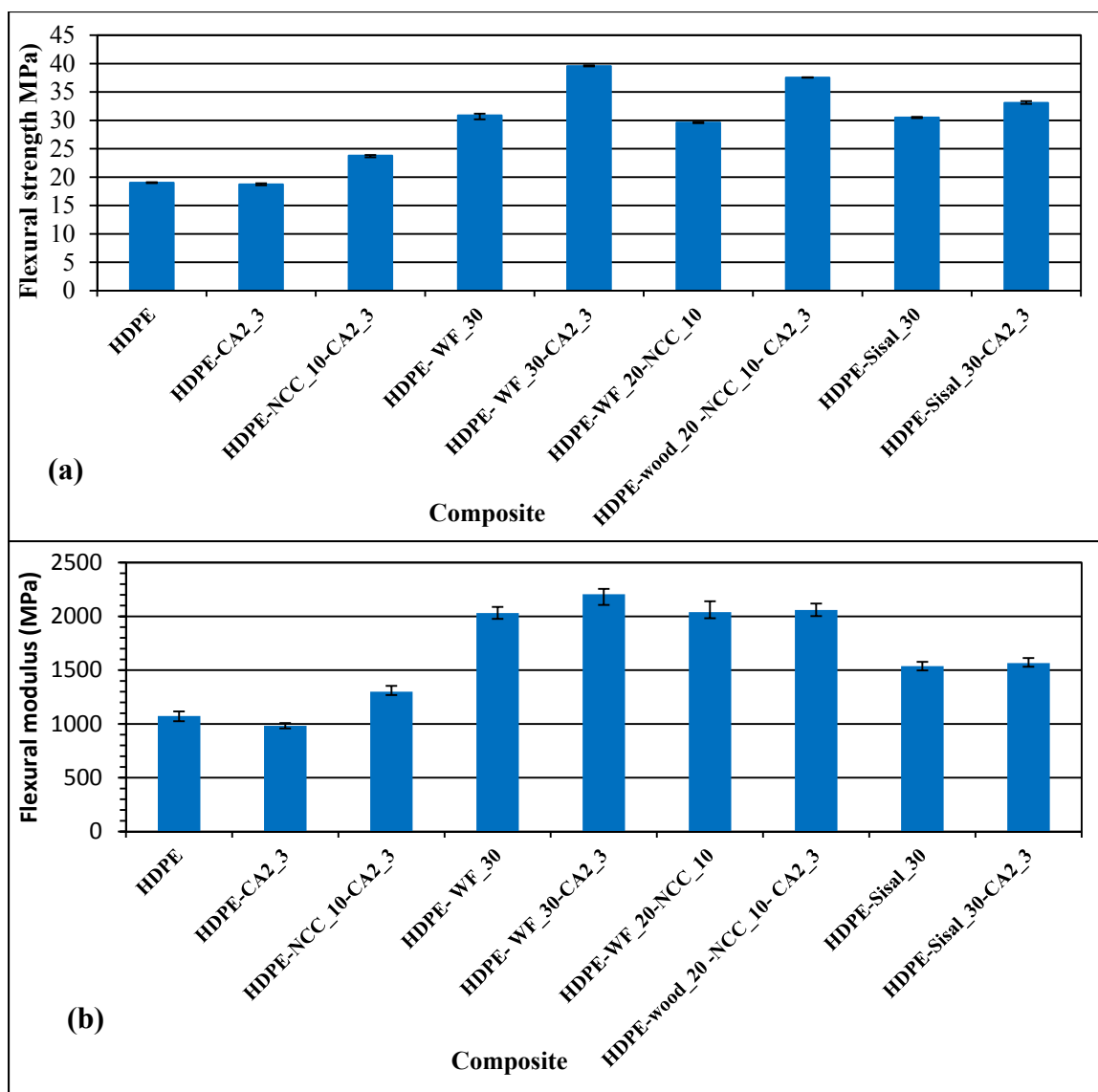


Figure 3.18 Effect of fiber types on the (a) flexural strength and (b) modulus of HDPE composite

As it can be observed in Figure 3.16, the compatibilizer agent has an important effect on flexural properties of different composites. Indeed, upon addition of 3 % of compatibilizer agent an increase of flexural modulus and strength was observed most likely due to the improvement of dispersion and interfacial fillers-matrix adhesion. For hybrid nanocomposite, adding of NCC had no significant effect to improve flexural properties of wood nanocomposite, contrariwise a small decrease of modulus and strength has been observed. So there was no synergetic effect between the NCC and wood flour which may be due to high

agglomeration of NCC. One solution for improving the dispersion of NCC is to provide a prior chemical surface modification before adding NCC on hybrid nanocomposite.

For tensile properties, the composite based an 30% wood flour presented a higher tensile properties with an increase of tensile modulus by 225% and tensile strength by 58% compared to neat polymer (see Figure 3.17). The decrease of tensile modulus by adding compatibilizer agent can be explained by the low effect of fiber matrix interaction at the beginning of tensile test where the nonlinear tensile stresses were lowest.

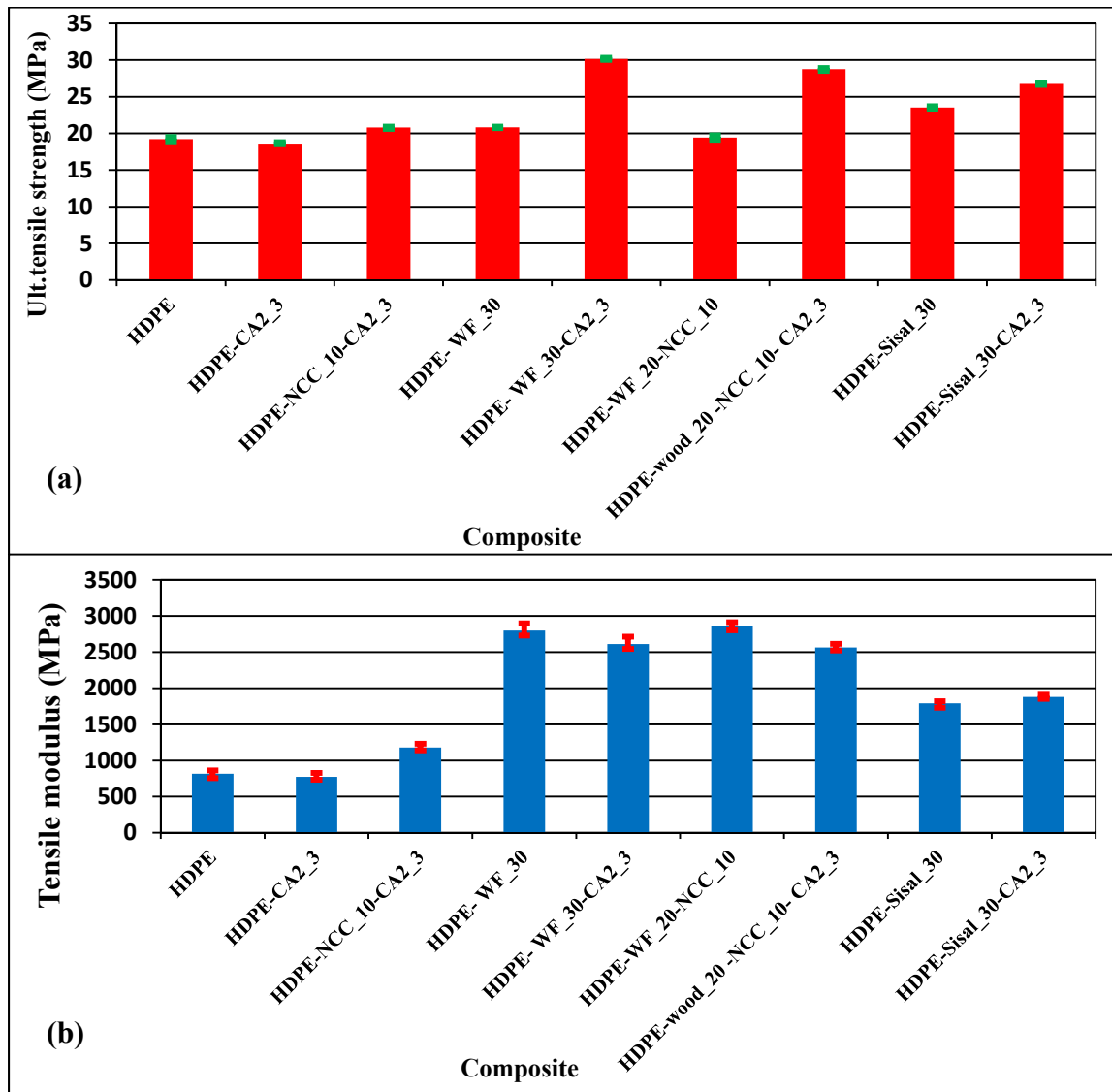


Figure 3.19 Effect of fiber types on the (a) tensile strength and (b) modulus of HDPE composite

3.2.2 Water Absorption uptake

The water absorption curves of various composites are shown in Figure 3.18. A comparison between the different fillers with or without the addition of compatibilizer has been investigated.

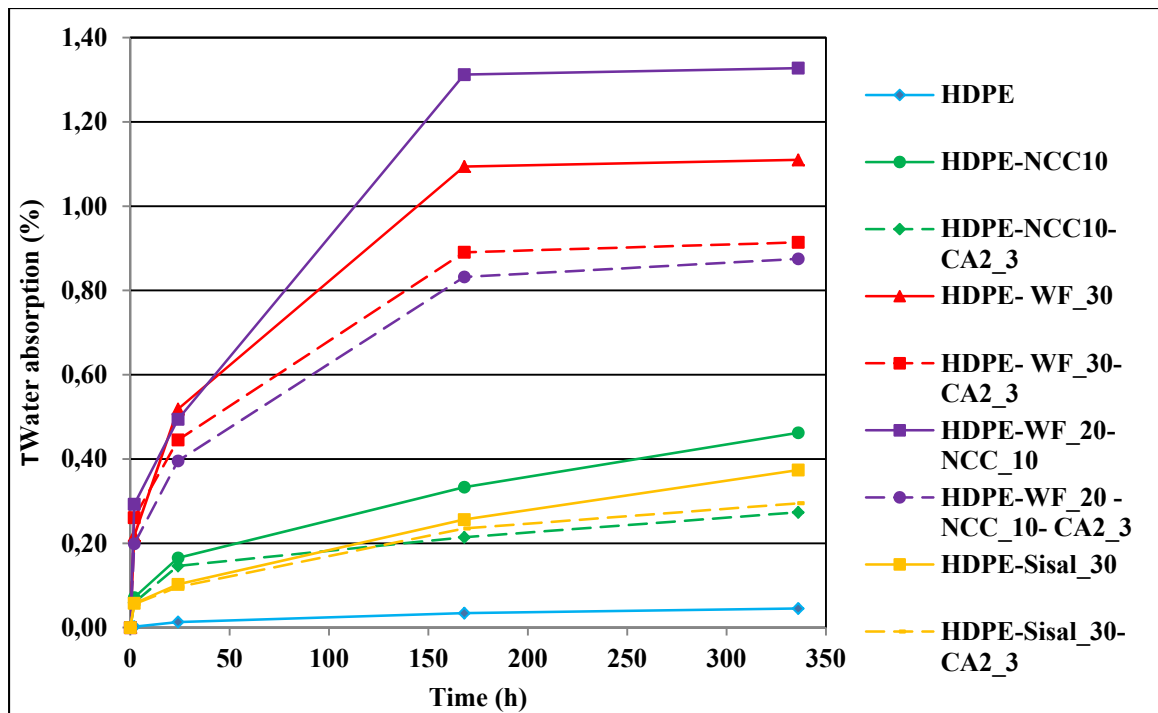


Figure 3.20 Effect of fiber types on water absorption of composites based HDPE

As it can be seen Figure 3.18, the higher moisture absorption was obtained with wood flour in comparison with sisal and NCC. Adding NCC in hybrid nanocomposite causes an increase of water uptake for wood/HDPE composite at the same fillers content. However, when 3% of compatibilizer agent was added the result was reversed and the hybrid composite proved a better moisture resistance that may be due to increase of NCC-HDPE interactions. Indeed, a compromise between the effect of the high surface area of NCC (high interaction with water molecules) and the more resistant chemical structure of crystalline cellulose compared to wood flour containing hemicelluloses can be occurred in the case of hybrid nanocomposites (Faruk, Bledzki et al. 2013). As a general trend, in all polymer composites, the addition of compatibilizer agent decreases the water absorption of immersed samples.

CONCLUSION

In this work, a successful experimental protocol to obtain NCC/HDPE nanocomposites was developed. Optimum temperature and processing condition were obtained with mixer processing temperature of 160° C, one step processing method and injection processing temperature of about 180°C. The results showed that adding up to 10% of NCC has no significant effect of torque values and the viscosity of polymer matrix which is beneficial to maintain the viscosity and melt behaviour of polymer.

Flexural tests were carried out to study the effect of adding NCC on the flexural strength and modulus of HDPE. Upon addition of 10 wt. % NCC there was an increase in about 26% of flexural strength and about 23% in flexural modulus were observed for composite containing 1% of CA2. The composition having high molecular weight compatibilizer (CA2) presented better results than that in the case of other compositions having low molecular weight compatibilizer (CA1). The same result was obtained by S. H. Kameshwari Devi (Devi, Shashidhara et al. 2010) for HDPE/nanoclay nanocomposite using different compatibilizer agents.

To improve the dispersion of NCC a different feeding technique based on the dispersion of NCC within water was tried. The microscopic observations indicated that this technique could be efficient to disperse the NCC within the HDPE. This method could be scaled up to test the mechanical properties of the samples.

Tensile characterization of the samples which presented the best flexural properties was carried out. Different concentrations of CA2 and CA1 were evaluated. Indeed, compared to pure HDPE, adding 1% compatibilizer agent CA2 proved resulted in an increase of tensile modulus of about 42% but no significant increase was observed for tensile strength. However, increasing the concentration of CA2 did not result in significant improvement of tensile properties.

The results of water absorption resistance indicated that the addition of compatibilizer was beneficial. For HDPE/NCC nanocomposite the water absorption is much lower when 3% of

CA2 was added. In fact, the water absorption uptake of nanocomposite with compatibilizer was reduced by 41%. In case of composite, the water uptake was larger for the samples presenting larger cellulosic particles such as wood flour and sisal.

Composites based on HDPE/Sisal and HDPE/wood flour to which NCC was added or not were also tested for the sake of comparison. The best mechanical properties (flexion and tensile) were obtained for wood flour composite by using of 3 % CA2. In fact, compared to neat HDPE, the flexural modulus and flexural strength were increased by 105% and 106 % respectively and the tensile modulus and tensile strength were enhanced by 225 % and 58 % respectively. These results proved that a good dispersion and interfacial interaction was obtained by addition of compatibilizer agent

RECOMMENDATIONS

Our study presents an initiation work to the development of hybrid composite materials based on wood fibers and nanocrystalline cellulose. As has been described, HDPE/NCC nanocomposite was successfully obtained with slight improvements of mechanical properties. However, the addition of NCC does not show any synergistic effect on HDPE/wood plastic composite.

So, additional research work is essential to explore more methods to improve NCC dispersion.

- Reduce the concentration of the NCC to add in the hybrid composite based on wood flour to have a better dispersion of NCC and see if synergistic effect can occur.
- Surface modification of NCC by ammonium quaternary salt to improve their dispersion and compatibility with HDPE.
- Introducing NCC suspension by liquid feeding directly in internal mixer.
- Trying different formulation of wood flour, NCC and maleic anhydride.

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