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## NUCLEATING EFFECT OF EXFOLIATED GRAPHITE NANOPLATELETS ON POLY(HYDROXYBUTYRATE) AND POLY(LACTIC ACID) AND THEIR NANOCOMPOSITES PROPERTIES

presented by

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# NUCLEATING EFFECT OF EXFOLIATED GRAPHITE NANOPLATELETS ON POLY(HYDROXYBUTYRATE) AND POLY(LACTIC ACID) AND THEIR NANOCOMPOSITES PROPERTIES

By

Dana Gabriela Miloagă

# A DISERTATION

Submitted to Michigan State University in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

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## ABSTRACT

## NUCLEATING EFFECT OF EXFOLIATED GRAPHITE NANOPLATELETS ON POLY(HYDROXYBUTYRATE) AND POLY(LACTIC ACID) AND THEIR NANOCOMPOSITES PROPERTIES

By

## Dana Gabriela Miloagă

Multifunctional polymer nanocomposites are attractive due to the multitude of properties that can be imparted to polymer matrices by the addition of small amounts of nanoparticles. Exfoliated graphite nanoplatelets (xGnP) represent a new nanosize reinforcing material that can lead to multifunctional polymer nanocomposites, and are a significantly less expensive alternative to other carbon nanomaterials (e.g. carbon nanotubes). The benefits of xGnP have been shown in nanocomposites made with several petroleum-derived thermoplastic polymers. Nanocomposites from biobased polymers and xGnP have not yet been investigated and are the object of this study.

This research is directed at understanding the interactions between xGnP and two polyesters derived from renewable resources, poly(3-hydroxybutyrate) (PHB), and polylactic acid (PLA). PHB and PLA are both semicrystalline polymers. Their properties largely depend on the degree of crystallinity, crystallization rate, and on the size and number of crystallites formed. For faster crystallization, important especially for dynamic processing conditions, both polymers often require the addition of nucleation agents. xGnP is shown to act as a nucleating agent, and to impart higher strength, modulus, thermal and electrical conductivity to these polymer matrices as well. Specifically, the research conducted covers two main aspects of the nucleating effect of xGnP on PHB and PLA: the rate of overall crystallization from the melt as a function of the amount of xGnP, and the influence of xGnP on the morphology and properties of the nanocomposites. A kinetic study of the PHB/xGnP crystallization, employing a modified form of the Avrami equation, revealed that the presence of xGnP increased the PHB crystallization temperature, as well as the crystallization rates. Optical microscopy and atomic force microscopy investigations revealed the reduction in the size of PHB spherulites. Nanocomposite properties were studied for PLA/xGnP systems, with a special focus on the relation between the nucleating effect of xGnP and improvement in modulus, and thermal conductivity. The results are particularly important since they may be applied to nanocomposites utilizing similar semicrystalline polymer matrices.

Copyright by DANA GABRIELA MILOAGĂ 2008 To my parents,

Leti and Ştefan Miloagă

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# **KEY TO SYMBOLS OR ABBREVIATIONS**

AFM	atomic force microscopy
BN	boron nitride
CNT	carbon nanotube
DMA	dynamic mechanical analysis
DSC	differential scanning calorimetry
HDPE	high density polyethylene
IL	ionic liquid
IL1	1-ethyl-3-methylimidazolium hexafluorophosphate
IL2	1-butyl-3-methylimidazolium hexafluorophosphate
IL3	1-butyl-4-methylimidazolium acetate
LS	light scattering
M-H-S	Mark-Houwnik-Sakurada
MWNT	multi-walled carbon nanotubes
nano-TA	nanoscale thermal analysis (scanning probe thermal analysis)
OM	optical microscopy
OMLS	Organically modified layered silicates
PDLA	poly(D-lactic acid)
PE	polyethylene
PEC	poly(e-caprolactone)
PET	poly(ethylene terephthalate)
PHA	poly(hydroxyalkanoate)
PHA	poly(3-hydroxyalkanoate)

PHB	poly(3-hydroxybutyrate)
PLA	polylactic acid
PLLA	poly(L-lactic acid)
PMMA	poly(methyl methacrylate)
PNC	polymer nanocomposites
POM	polarized light optical microscopy
PP	polypropylene
PVC	poly(vinyl chlorite)
Stdev.	Standard deviation
SWNT	single-walled carbon nanotubes
TEC	triethyl citrate
ТМА	thermomechanical analysis
RTIL	room temperature ionic liquids
xGnP	exfoliated graphite nanoplatelets
xGnP-1	exfoliated graphite nanoplatelets of 1 mm diameter (average)
xGnP-15	exfoliated graphite nanoplatelets of 15 mm diameter (average)
XPS	X-Ray Photoelectron Spectroscopy

## **CHAPTER 1**

## **INTRODUCTION AND BACKGROUND**

#### Current trends in polymer nanocomposites

Polymer nanocomposites (PNC), obtained by incorporation of nanosize particles into polymer matrices, have attracted a substantial research interest from academic and industrial organizations during the past decade.<sup>1-3</sup> Small amounts (up to 5 % vol) of nanosize particles – spheres, rods, or platelets – were shown to substantially modify the properties of both thermosets and thermoplastics, revealing advantages particularly for applications requiring enhanced properties and light weight.

## Market trends and applications

According to a market research study performed by The Freedonia Group, Inc., a Cleveland-based industry research firm, by 2010 the nanocomposites demand will grow to nearly 350 million pounds per year, and will rise to over seven billion pounds with a value nearing \$15 billion by 2020. Simultaneously, thermoplastic polymers are estimated to account for eighty percent of the

predicted total demand for PNC in 2020.<sup>4</sup> In the shorter term, the report estimates that demand growth will be fastest in higher-priced resins such as engineered plastics and thermoplastic elastomers, as much of the initial demand for nanocomposites will be in higher-end applications. Eventually, polymer nanocomposites based on commodity plastics, such as polypropylene (PP), polyethylene (PE), poly(vinyl chloride) (PVC) and polyesters are expected to dominate the market. An emerging area will be nanocomposites from biobased polymers, which are of significant importance considering the general effort to reduce the amount of plastic waste generated, and the recent focus on biodegradable polymers as potential alternatives to traditionally used materials like polyethylene terephthalate (PET) and polyolefins.<sup>5</sup>

Organically modified layered silicates (OMLS) and carbon nanotubes (CNT) continue to dominate the market, with OMLS being extensively studied for applications in the packaging industry. OMLS added to polymers can impart enhanced stiffness at low addition levels, can improve barrier properties, heat distortion temperature, and flame-retardancy of polymer matrices, producing nanocomposites with commercial applications in a variety of diverse markets ranging from automotive to packaging.<sup>6</sup> In addition to improving mechanical properties, CNT and carbon-based nanoreinforcements distinguish themselves by their ability to impart thermal and electrical conductivity to polymers.

The automotive industry is still leading the way in nanocomposite application development<sup>3;7</sup>, with electrically conductive PNC becoming preferred materials for fuel delivery lines, traditionally made from steel. Hyperion Catalysis

International estimates that 60 % of the cars produced in the United States in 2007 incorporated their multi-walled carbon nanotubes (MWNT) composites in fuel lines to prevent the accumulation of static electricity.<sup>7</sup> Electrically conductive materials incorporating CNT were also developed for coatings used in exterior body panel applications. Higher-end applications in the automotive industry include batteries, fuel cells, energy storage materials, and materials for electromagnetic and radiofrequency shielding.

The electronics and medical areas are two other sectors largely developing PNC requiring improved electrical and thermal conductivities, for applications ranging from thin-film capacitors in integrated circuits, solid polymer electrolytes for batteries, nanoscale switches and sensors, and minimally invasive diagnosis devices.

There is a strong need for PNC with enhanced thermal and electrical conductivity, and nanosize reinforcements that can be alternatives to the still highly-priced CNT are highly desired.

#### Design challenges and recent research focus

Regardless of the type of nanosize reinforcements, the challenges in PNC differ from common challenges encountered in traditional composites. Dimensional similarities between physical characteristics of polymers (such as radius of gyration and lamellar thickness) and nanosize reinforcing particles lead to the necessity to go beyond filled systems<sup>8</sup> and explore in detail polymer-particle interactions responsible for the improved properties of PNC.

Such interactions, together with the use of external forces and gradients during processing, are more likely to be responsible for the properties of PNC than dispersion and alignment – significant factors considered in composites containing micron-sized fillers.

The success achieved by Toyota in the 1980s with Nylon/clay nanocomposites<sup>9;10, 11</sup> set the benchmark for the use of OMLS for improving mechanical, thermal and physical properties of polymer matrices by controlling the exfoliation of clay layers. Earlier research on nanocomposites incorporating OMLS was directed predominantly at the understanding of dispersion and exfoliation of nanoplatelets. Important research was also focused on processing methods for PNC, from *in-situ* polymerization to polymer intercalation from solution and polymer melt intercalation. It was in the late 1990s and early 2000s when a large number of research groups directed their attention to modifications induced by OMLS nanoplatelets to the crystalline structures of the host polymers. Polymorphism was investigated in relation to incorporating OMLS in Nylon<sup>12;13;14-17</sup>, syndiotactic polystyrene<sup>18</sup>, poly(vinyl alcohol) (PVA)<sup>19</sup>. At the same time, with nanoscale morphological characterizations becoming more accessible through transmission electron microscopy (TEM), atomic force microscopy (AFM), and wide angle X-ray diffraction (WAXD), the effects of OMLS on the shape and size of crystallites formed by various polymers was also an important research field. Reports on the crystallization, properties, and crystal and nanoscale morphology of PET/OMLS nanocomposites were published as early as 1999. Concomitant work reported by Nam et al.<sup>20</sup> investigated the

hierarchical structure of the PP/OMLS systems using wide-angle X-ray diffraction (WAXD), small-angle X-ray scattering (SAXD), TEM, polarizing light optical microscopy (POM) and light scattering (LS), focusing on the modifications of PP lamellar thickness and spherulitic structure.

By 2005, it was evident that for semicrystalline polymers nanocomposites polymorphism, changes in crystallites shape and size, as well as modification of the time required to achieve maximum crystallinity were general effects resulting from the addition of nanoparticles to polymers.<sup>21</sup>

During the last five years, the physical aspects of PNC related to polymer behavior when subjected to confinement by the presence of nanoparticles with surface and the specific interactions large area. occurring at polymer-nanoparticles interfaces were key issues<sup>3, 22</sup>. The contribution of polymer-particle interfaces to the properties of the nanocomposites increases as the number of the reinforcing particles increases. The interface and the interaction between particles dominate the macroscopic properties.<sup>3</sup> For example, in case of platelets of diameter d and thickness h (Figure 1.1), supposing that the thickness (t) of interfacial layer that surrounds the particle is independent of the size of the particle, the relation between the particles' contribution and the interface's contribution to the bulk properties of the nanocomposites is given by Equation 1.1.

$$\frac{V_{\text{interface}}}{V_{\text{particle}}} = \frac{2\pi \frac{d}{2} \left(\frac{d}{2} + h\right) t}{\pi \left(\frac{d}{2}\right)^2 h} = \frac{2t}{h} \left(1 + \frac{2h}{d}\right)$$
(1.1)



Figure 1.1 Schematic of the contribution of interfacial layer to the properties of PNC

In a recent review<sup>8</sup>, Vaia and Maguire emphasized the opportunities afforded by the ability to control nanoparticles hierarchy, and underlined the two general approaches to this challenge: a) external-in (directed patterning of nanoparticles dispersion), and b) internal-out (mesophase assembly of nanoparticles).

One general trend in currently designed PNC involves careful evaluation of polymer-particle interface, and the use of chemical and physical methods to alter the interface and thus control material properties.

## **Description of the present study**

## Context and motivation

The diversity of PNC is dramatically increasing as new nanosize reinforcements are developed, and as the list of polymer matrices is longer limited to PP and Nylon, as in the early years of PNC. The types of polymer matrices expanded, including a large variety of epoxies, engineered thermoplastics and liquid crystalline polymers.

In the fast-developing research on PNC, during the last ten years there has been intensive research on biobased, biodegradable polymers as matrices, especially for composites with OMLS, in order to reduce the effects of plastic waste on the environment. The United States generates more than 14 million tons of plastic waste annually<sup>23, 24</sup>, only 28 % of which is recycled at a cost of several million dollars<sup>25</sup>. According to the principles of green chemistry, there is a need for polymeric materials whose production would not involve the use of toxic products, and that could be degraded to natural, nontoxic products.

The transition to biobased materials will be enhanced if new and desirable attributes can be added to their intrinsic properties. In addition to an increasing demand for PNC with high mechanical properties, materials with improved thermal and electrical conductivity are increasing in importance, so imparting electrical and thermal conductivity to biobased polymer matrices is of great interest.

The exfoliated graphite nanoplatelets (xGnP) developed in the Drzal Group at Michigan State University represents a novel attractive carbon-based nanosize material which when added to and dispersed within polymers at a concentration of a few percent, adds multifunctionality as well. While significantly less expensive than other carbon nanomaterials (e.g. CNT), xGnP were already shown to be comparable to those when used in nanocomposites with several petroleum-derived thermoplastic polymers, such as Nylon<sup>26</sup> and PP.<sup>27-30</sup>

Nanocomposites from biobased polymers and xGnP have not been investigated, though they are particularly attractive for applications ranging from structural materials to substrates in electronics, advanced energy sources, and even biomedical applications such as tissue engineering, bone implants and bone growth stimulation, which require biocompatible materials with enhanced mechanical properties<sup>31</sup> and improved conductivity.

## **Objective**

It is the objective of this study to identify and characterize the effects of the exfoliated graphite nanoplatelets on the crystallization of poly(hydroxybutyrate) (PHB) and polylactic acid (PLA) polymers and the properties of their resulting nanocomposites.

## Approach

For semicrystalline polymer matrices, the nucleation by nanoparticles is one particular interaction that affects the polymer crystallization and further the properties of the resulted nanocomposites.

PHB and PLA are both semicrystalline polymers derived from renewable resources. Their properties largely depend on the degree of crystallinity, crystallization rate, as well as on the size and number of crystallites formed. For practical applications requiring fast achievement of maximum crystallinity, both these biobased polymers often need to incorporate nucleation agents. xGnP can not only act as a nucleating agent, but has the potential to impart higher strength, modulus, heat resistance, better barrier properties, and electrical conductivity to polymer matrices.

This study investigates the fundamental interactions between PHB, PLA, and the graphene surface of xGnP. Once an understanding of how the xGnP affects the crystallization behavior and nanoscale structure of the polymers is obtained, insights into how this interaction at the nanoparticle level affects the resulting nanocomposite properties can be attained. The outcome of the study is of importance for semicrystalline polymers in general.

#### Background on nucleation of semicrystalline polymers

One common feature of the thermoplastic polymer matrices used in nanocomposites, regardless of their production from petroleum or from natural resources, is their semicrystalline nature. The crystalline state is commonly defined as one that diffracts X-ray and exhibits a first-order transition known as melting.<sup>32</sup> Upon cooling from the melt state, crystalline polymer crystals nucleate and grow.

## The importance of nucleation for semicrystalline polymers

During melt processing of semicrystalline polymeric materials, depending on cooling and shear conditions, complex morphologies develop and these determine the mechanical properties of the materials obtained. For dynamic applications such as injection molding, faster crystallizing polymers are ideal candidates.

Certain requirements must be fulfilled in order for a polymer to crystallize.<sup>33</sup> The molecular structure of the polymer should be regular enough to allow the crystalline ordering; the crystallization temperature should be below the melting temperature, but not too close to the glass transition temperature of the polymer; nucleation must occur prior to crystallization, and the crystallization rate should be sufficiently high. Controlling the nucleation is an essential tool for manipulating the morphology and thus controlling the material properties.

A basic classification of the nucleation processes in a polymer melt divides them into homogeneous, when the melt is free of extrinsic entities, and heterogeneous, in which case nucleation occurs in the presence of foreign surfaces in the pure polymer melt. Nanosize reinforcement particles in polymer composites have been shown to act as heterogeneous nucleating agents in several semicrystalline matrices.<sup>34-37</sup>

#### The heterogeneous nucleation of crystalline polymers

Heterogeneous nucleation processes are commonly described in terms of a free energy balance between the formation of a new crystal and new surface(s) associated with it.<sup>38,39</sup> Initially, there is an increase in free energy associated with the formation of nuclei smaller than a critical size. Because the newly-formed crystalline phase is small, the interfacial energy ( $\Delta G_{surface}$ ) increases the total free energy ( $\Delta G$ ) to a larger extent than the free energy accompanied by the phase transformation ( $\Delta G_{C}$ ) lowers it.<sup>38</sup> The system remains in thermodynamically unfavorable state until the free energy reaches a maximum, and then decreases and becomes negative, leading to stable nuclei (Figure 1.2)<sup>38</sup>.

Homogeneous nucleation is rarely observed for most of the crystalline polymers, since the presence of any foreign substrate (usually impurities, unmelted polymer, remaining catalysts, or reinforcing particles – in case of polymer composites) alter the surface energy contribution to the free energy.

In order to control the heterogeneous nucleation, one needs to understand the factors governing the process. The heterogeneous nucleation relies on the presence of foreign surfaces in the polymer melt (e.g. nucleating agents) that reduce the free energy opposing primary nucleation ( $\Delta G_H$ ), increasing the rate of nucleation, and the rate of crystallization. The free energy opposing primary nucleation defined<sup>38</sup> in Equation 1.2.



Figure 1.2 Schematic representation of primary nucleation

$$\Delta G_{H} = \frac{16 \cdot \Delta \gamma \cdot \gamma \cdot \gamma_{\theta} \cdot T_{m}^{2}}{(\Delta H \cdot \Delta T \cdot \rho_{c})^{2}}, \qquad (1.2)$$

where  $\Delta \gamma$  is the specific interfacial free energy difference parameter that accounts for one surface containing the melt and one surface containing the heterogeneous nucleus, and  $\gamma$  is its side surface free energy. The most important parameters affecting the heterogeneous nucleation are supercooling

(the difference between the melting temperature and the temperature of crystallization from the melt), and the specific interfacial free energy parameter. As the primary nucleation in proportional to  $1/\Delta T^2$ , the higher the supercooling, the faster the crystallization process takes place. Nucleating agents are more effective as the specific interfacial free energy parameter,  $\Delta \gamma$ , is smaller. A smaller  $\Delta \gamma$  ensures a smaller free energy barrier opposing the nucleation process. Other parameters affecting the heterogeneous nucleation are the thermal history of the polymer, and epitaxy.<sup>38</sup> The thermal history is particularly important since the presence of non-melted polymer particles that may act as nuclei is largely depending on melting temperature, melting time, as well as on the temperature of previous crystallization. Epitaxy, on the other hand, is related to crystallographic similarities between the topography of the polymer and the surface topography of nucleating agent, and is still considered the main physical process explaining the nucleating capability of nucleating agents. This aspect will be discussed later in this study, with a focus on PHB and PLA.

## Nucleating agents for semicrystalline polymers

The addition of nucleating agents to semicrystalline polymers has two important effects. First, nucleating agents affect the kinetics of crystallization: the overall rate of crystallization of the polymer increases, leading to faster solidification of the polymer melt upon cooling, which enhances processability. Second, the nucleating agents affect the polymer morphology, by diminishing the

average spherulite size, which modifies the mechanical and optical properties of the nucleated polymer.<sup>38,39</sup> In PNC, the nanosize particles were shown to act as nucleating agents in various thermoplastic-based systems. The mechanism of nucleation, and the effects on the polymer properties are largely depending on the size and nature of the nucleating agents, and are different for nanosize particles than for the traditional nucleating agents.

Nucleating agents do not affect all semicrystalline polymers to the same extent. To be sensitive to nucleating agent, a polymer's crystallization rate has to be not too high (as, for example, high density polyethylene (HDPE)), in which case the growth would occur on the formed polymer crystals, regardless of the presence of the nucleating agent in the melt, but not too low either (e.g. polycarbonate – an amorphous polymer).

The general requirements for good nucleating agents are: to contain both an organic and an inorganic group, to be well dispersed in the polymer, to be insoluble or able to become insoluble in the polymer, to have an epitaxial match with the polymer crystal, or to chemically react with the polymer generating a product that can nucleate (*in-situ* generation of a nucleating agent).<sup>38</sup>

The nature of nucleating agents can be very diverse. Impurities (such as catalyst residues), organic compounds, for example benzoic acid, and saccharine<sup>40, 41</sup>, and inorganic compounds, such as talc and pigments, can all nucleate crystalline polymers.<sup>38;39</sup>

PP, polyamides, PET are extensively modified by using nucleating agents.<sup>42</sup> The optimum content of nucleating agents varies for different polymers, but is

usually below 1 %, depending on the crystallization behavior of the polymer. Polypropylenes, for example, have intermediate crystallization rates, and are being studied to establish structure-properties relationships and to compare the effects of various nucleating agents. Examples of traditional nucleating agents for polypropylenes are talc, aluminum salts of dibenzylidene sorbitol derivatives,<sup>43,44,38</sup> 4-biphenyl carboxylic acid, thymine, dibenzyliden sorbitol, sodium benzoate.<sup>38</sup>

## Efficiency of nucleating agents

The conventional method used to characterize the efficiency of nucleating agents is differential scanning calorimetry (DSC). Two parameters determined using this thermal analysis method are essential for describing the crystallization in the presence of nucleating agents: the crystallization temperature ( $T_c$ ), which is the peak temperature of the crystallization exotherm, and the crystallization half-time calculated at a fixed crystallization temperature. Nucleating agents are thus more efficient if a polymer's  $T_c$  shifts to higher values in their presence, and respectively if the crystallization half-time is lower for the nucleated polymer than for the neat polymer. For the purpose of comparing various nucleating agents, Fillon et al<sup>45</sup> defined the nucleation efficiency by establishing a scale for describing the nucleation ability. The lower limit is defined by the neat, non-nucleated polymer, while the upper limit is set by the wholly self-nucleated polymer. The upper limit was set considering that the crystal fragments produced in self-nucleation satisfy three criteria that characterize an ideal

nucleating agent: ideal concentration (i.e. highest achievable), ideal dispersion in the molten polymer, and ideal polymer-"substrate" interaction (since the polymer and the "nuclei" have the same chemical composition and crystal lattice). In this context, the nucleation efficiency (NE) was defined<sup>45</sup> as follows (Equation 1.3):

$$NE = \frac{T_{c,NA} - T_{c1}}{T_{c2,max} - T_{c1}} \times 100, \qquad (1.3)$$

where  $T_{c,NA}$  is the crystallization temperature of the nucleated polymer;  $T_{c1}$  is the crystallization temperature of the neat polymer, and  $T_{c2,max}$  is the crystallization temperature of the self-nucleated polymer.

#### Effects of nucleating agents

The addition of nucleating agents to crystalline polymers has two main effects. The first effect is on the kinetics of crystallization: the rate of overall crystallization increases. The other effect concerns the polymer morphology, and consequently the mechanical, optical, and barrier properties.

*a)* Effects on the kinetics of crystallization. Figure 1.3 shows how the heat of fusion, directly proportional with the degree of crystallinity of a PP (PP), is higher for talc-filled PP than for calcium carbonate-filled PP. Also, the heat of fusion increases as the volume fraction of the filler increases.<sup>46</sup>


**Figure 1.3** Effect of nucleating agent type and content on the crystallization temperature of PP matrix. (o)  $CaCO_3$ ; ( $\Delta$ ) talc

Figure 1.4 shows a comparison of the nucleating effect of four agents on PP,

as well as the dependence of the crystallization temperature on cooling rate.<sup>44</sup>



**Figure 1.4** Dependence of the crystallization temperature on the cooling rate for PP, and PP containing CaCO<sub>3</sub> (CC), talc (TC), p-tert-dibutyl benzoic acid monohydroxy aluminium (BA), and p-dimethyl-benzylidene sorbitol (GA)

The highest crystallization temperatures for nucleated PP were recorded in the systems incorporating an aluminum-containing organic compound, followed by PP nucleated by a small organic molecule, p-dimethyl-benzylidene sorbitol (GA), and talc-nucleated PP.

Effects on morphology. Upon addition of nucleating agents, the size and b) number of spherulites decreases, and this affects the mechanical and optical properties of the nucleated polymer. For example, talc, largely used for the modification of PP, has platelet geometry, and a strong nucleating effect.<sup>47,46</sup> The addition of talc particles to molten polypropylenes was shown to increase mechanical properties such as flexural strength, hardness, and impact strength, as well as thermal properties (heat distortion temperature). Optical properties are also affected by the addition of traditional nucleating agents, since the spherulites formed are smaller in size than in case of the neat polymers. Such nucleating agents that reduce haze and increase the transparency of semicrystalline polymers are commonly referred also as clarifying agents<sup>48,42</sup>. In case of polypropylenes, dibenzyliden sorbitol derivatives can be very well dispersed in the matrix, and have such a nucleating effect. All clarifying agents are nucleating agents, but not all nucleating agents are clarifying agents (Figure 1.5).<sup>42</sup>



**Figure 1.5** Behavior of nucleating and clarifying agents

Pukanzky et al.<sup>46</sup> studied the morphology and properties of particulate filled polymers and attempted to elucidate the extent at which the nucleating effect affects the polymer properties. This group also underlined the existing controversy regarding the relationship between aspects of the crystalline morphology a polymer properties. By comparing PP/CaCO<sub>3</sub> and PP/talc systems, they showed that talc, which has a nucleating effect on PP, determines changes in crystallization and in mechanical properties very different from the changes induced by calcium carbonate, at the same loading.

Another aspect regarding the effects of nucleating agents on the properties of the modified polymers is related to the thermal conductivity of the nucleation additive. Radhakhrisnan et al.<sup>49</sup> observed that in case of PP, the higher the thermal conductivity of the filler, the faster the cooling rate, and the lower the

crystallinity value. In the same study, the thermal conductivity of the filler was reported to affect the skin-core type of morphology of molded products.

For traditional nucleating agents, the extent of the nucleating effect depends also on the particle size of the nucleating agent. Pukanszki et al.<sup>46</sup> showed this correlation in case of PP/talc systems (Figure 1.6). It is almost unanimously accepted that the strength and the impact resistance of filled polymers depends largely on the particle size of the fillers. Smaller particles tend to aggregate more, which is detrimental for the mechanical properties. Aggregation occurs below a certain particle size or above a certain specific surface area. The critical size depends on processing conditions and illustrates the importance of attaining a high degree of dispersion without aggregation.



Figure 1.6 Effect of the size and amount of talc particles on PP

In terms of techniques utilized to monitor changes in polymer morphology determined by nucleating agents, optical microscopy (OM) is a visualization technique that has been largely used to observe the changes in polymers' spherulitic structures. AFM is now routinely used to study the surface morphology and nanostructure of crystalline polymers and polymer composites,<sup>50,51,52</sup> offering insights into processes such as crystallization, crystal thickening and crystal deformation, phenomena which can also be observed *in situ*.<sup>50</sup> Changes in crystallinity are usually monitored using WAXD, while small angle X-ray diffraction methods (SAXD) may be employed to determined changes in the fine lamellar structure.

### Factors that reduce crystallinity in polymers

External factors such as the nature of solvents or solvent mixtures in case of crystallization from solution, or temperature, pressure, and crystallization time in case of crystallization from the melt are known to be controllable to a certain extent for achieving designed degrees of crystallinity in polymer samples. When inhibiting the crystallization is a goal, strategies include blending with partially miscible amorphous polymers<sup>53</sup>, or incorporating additives with specific surface active groups that bind to nascent crystals and frustrate crystallization mainly by acting as defects along the polymer backbone.<sup>54, 55</sup>

Of particular interest for the present study are geometrical confinement effects leading to reductions in crystallinity. Observation of crystallization of PET droplets in an amorphous polycarbonate matrix<sup>56</sup> indicated that PET crystallizes

differently in bulk than it does when surrounded by the amorphous phase, which stops crystallization. The finer the dispersion of PET, the greater the inhibition of crystallization. Similar inhibition of crystallization processes, resulting in a decrease of the degree of crystallinity, was observed in polymer composites consisting of alternating layers of two or more polymers (multilayer polymer films). During the last decade, materials were described where the thickness of polymer layers varies from micron-size to nanosize.<sup>57</sup> The layer thickness affects the physical properties of the polymer<sup>58-61</sup> and its ability to undergo thermal transitions. When semicrystalline polymer layers are as thin as a few tens of nanometers<sup>57</sup>, confinement of the polymer generates transparent layers, since no micron-scale structures can be formed.

Nanoscale confinement effects resulting in inhibition of crystallization, as well as in modification of glass transition temperature, were also observed in PNC, for example containing OMLS<sup>62-64</sup>, or CNT<sup>65</sup>. In such nanocomposites incorporating high-modulus, rigid nanoparticles, as the amount of particles in the polymer matrix increases, the distance between particles decreases, and more polymer chains are confined. This entrapment was described as polymer sandwiched between two hard walls<sup>66</sup>, and an analogy was made with thin polymer films. Modeling and understanding of the behavior of confined polymers were more successful in predicting changes in glass transition temperature and their dependence on thickness of polymer film/interparticle spacing.<sup>67, 68</sup> When the nanosize particles provide nucleating centers for the polymers, the confinement leads to inhibition of crystallization. The growth of spherulitic structures is

stopped, and bi-dimensional crystalline entities are formed, as seldom proven by systematic studies of crystallization behavior. Ferreiro<sup>69, 70</sup> reported the formation of irregular dendritic structures in OMLS/polymer blends and a year later, Gránásy et al.<sup>71</sup> described the formation of "dizzy dendrites" using a phase-field theory, in which randomly distributed foreign particle inclusions perturb the crystallization by deflecting the tips of the growing dendrite arms. Recently, in a study regarding HDPE/CNT, Trujillo et al.<sup>72</sup> reported that high CNT loadings lead to a decrease in polymer crystallinity, longer crystallization time, and sharp decrease of Avrami exponent for isothermal crystallization. The Avrami exponent calculated for low amounts of CNT in HDPE was between 1.94 and 2.2, corresponding to three-dimensional spherulitic structures, and dropped dramatically as the CNT loading was increased. Such low values are commonly attributed to one-dimensional and two-dimensional crystal structures. Similar effects are described further in this thesis (Chapters 3 and 5).

#### Nanoparticles nucleating semicrystalline polymers

The traditional nucleating agents used for the modification of semicrystalline polymers are usually micron-sized. As PNC research developed, numerous nanoparticles used as reinforcements in polymer matrices were shown to act as heterogeneous nucleating agents for the polymers. In essence, both nano- and micron-size particles are heterogeneous nucleating agents. The main difference is due to the size effect, largely discussed in relation to the mechanical properties

of polymer composites, which plays a significant role in the early stages of nucleation, since it is related to important modifications of morphology.

It has been shown<sup>35;34, 73;74</sup> that nanoparticles can be used as structure and morphology directors, for example for stabilizing a metastable or conventionally inaccessible polymer phase<sup>75</sup>, or to induce new energy dissipation mechanisms.<sup>76</sup>

In terms of processing, it is important to notice that, as opposed to phase separation – occurring in case of incorporating micro-sized fillers in polymers –, as the size of the fillers in the polymer matrices decreases, dispersion and agglomeration become key problems to be overcome in obtaining high-performance polymer composites.

Polymer materials containing nanoparticles have different failure mechanisms. As the size of the fillers decreases, the materials no longer fail due to debonding, which is the deformation mechanism predominating in composites containing large particles; cracks are initiated inside aggregates forming upon addition of particles having small size.<sup>77</sup>

A novel application of the nucleating effect of nanoparticles (namely OMLS) on polymer blends was reported recently by Si et al.<sup>78</sup> OMLS were shown to act as compatibilizers in polymer blends, due to their extremely large surface area and to their ability to become very effective nucleating agents for *in-situ* graft formation during melt mixing. An increased compatibility due to the localization of OMLS particles at the interface was demonstrated for polystyrene/poly(methyl

metacrylate) blends, reflected in the increase of the modulus of the blend, and easier recyclability.

According to Ray, et al.<sup>79</sup>, the polymers' biodegradability can be affected by the incorporation of nanoparticles. Organically modified layered silicates (OMLS)/PLA were shown to degrade faster when the OMLS were well-distributed in the polymer matrix. The authors hypothesized that as maximum parts of the matrix are in contact with the clay's edge and surface, there is a higher tendency of the polymer chains to fragment than in case of poor dispersion of the nanoparticles. To our knowledge, correlations between the rate of biodegradability and the dispersion of micro-sized fillers and/or nucleating agents were not reported. The potential effect on the rate of degradation is another unique feature of nanosize materials, again due to the size similarity between the nanoparticles and the polymers' nanoscale structure.

Besides the OMLS, that were proved to nucleate semicrystalline polymers, and to promote different polymorphs, affecting the properties of the resulted nanocomposites, another significant class of nanosize particles largely investigated is represented by CNTs. Various forms of CNT were shown to nucleate crystalline polymers. Several research groups investigated the nucleating effect of single-walled carbon nanotubes (SWNT) on PP<sup>80</sup>,<sup>65</sup> Grady et al. showed that the SWNT changed the kinetics of both isothermal and nonisothermal crystallization, in a manner similar to carbon fibers. The amount of SWNT required to nucleate PP was found<sup>80</sup> to be 0.6 % wt, at which loading the number of nucleation sites increased up to the point that more SWNT did no

longer increase the number of crystallites. The very low amount confirmed that the number of nucleated crystals was proportional to the surface area of the nucleating agent. Recently, CNT were showed to nucleate poly(hydroxyvalerate-co-hydroxybutyrate)<sup>81</sup>, PVA<sup>82</sup>, PLA<sup>31</sup>, PET<sup>83</sup>, HDPE<sup>84</sup>, Nylon-6<sup>85</sup>, Polyamide 1010<sup>86</sup>.

## Nanocomposites based on biodegradable polymers

Biodegradable polymers are defined as polymers that undergo microbially induced chain scission leading to mineralization.<sup>87</sup> Such polymers can be derived from petroleum sources or can be obtained from mixed petroleum and biomass-derived products. A classification of biodegradable polymers is presented in Table 1.1.

Biodegradable polymers obtained from biologically based feedstock are especially attractive since these reduce the reliance on polymers derived from depleting natural resources. In the fast-developing research on PNC, during the last ten years there has been an intensive research on biodegradable polymers as matrices, especially containing OMLS reinforcements.

Natural polymer <del>s</del>		Synthetic polymers	
Sub-classification	Examples	Sub-classification	Examples
1. Plant origin		1. Aliphatic polyesters	
1.1. Polysaccharides	cellulose, starch,	1.1. Glycol and	poly(ethene succinate),
	alginate	dicarbonic acid	poly(butylenes
		polycondensates	terephthalate)
2. Animal origin		1.2. Polylactides	polyglycolide,
			polylactides
2.1. Polysaccharides	chitin (chitosan),	1.3. Polylactones	poly(ε-caprolactone)
	hyaluronate		
2.2. Proteins	collagen, albumin	1.4. Miscellaneous	poly(butylenes
			terephthalate)
3. Microbial origin	· · · · · · · · · · · · · · · · · · ·	2. Polyols	poly(vinyl alcohol)
3.1. Polyesters	poly(hydroxyalkanoates)	3. Polycarbonates	poly(ester carbonate)
3.2. Polysaccharides		4. Miscellaneous	polyanhydrides,
			poly(a-cyanoacrylate)s,
			polyphosphazenes,
			poly(orthoesters)

## Table 1.1 Classification of biodegradable polymers

# Poly(hydroxybutyrate) and polylactic acid polymers

One group of biodegradable polymers that has received considerable attention is the poly(hydroxyalkanoates) (PHAs),<sup>89, 90</sup> which are thermoplastic biopolyesters typically synthesized by various bacteria and microorganisms that use them as reserves of carbon and energy.<sup>89-91</sup> Materials produced from PHAs can be totally biodegraded under aerobic and/or anaerobic conditions <sup>89-94</sup> at the

end of their lifetimes. Figure 1.7 shows the chemical structure of PHAs. In PHB, the side group is  $CH_{3}$ .



Figure 1.7 Chemical structure of PHAs

Polylactic acid or polylactide is a biodegradable, thermoplastic, aliphatic polyester derived from lactic acid. PLA is commonly produced in a high molecular weight by ring-opening polymerization of lactide (Figure 1.8).

Several forms of PLA exist, and the variety is due to the chirality of the lactic acid. Poly-L-lactide (PLLA) is the product resulting from polymerization of lactid acid in the L form. PLLA has a crystallinity around 37 %, a glass transition temperature between 50 and 80° C and a melting temperature between 173 and 178° C. The polymerization of a mixture of both L and D forms of lactic acid leads to the synthesis of poly-DL-lactide (PDLLA) which is not crystalline but amorphous.



Figure 1.8 Synthesis of polylactides

PHB and PLA are two of the most investigated biodegradable thermoplastic polymers derived from natural resources. They are both semicrystalline in nature, and can be processed using conventional polymer processing methods, where it is desired that the polymers crystallize fast from the melt. One way to ensure fast crystallization is to incorporate nucleating agents or reinforcements that could help control the crystallization rate. Similar to traditional thermoplastic, the expected effects after adding nucleation agents are: improvement of processing cycle or spinnability, improvement in transparency of molded articles, improvement of rigidity of molded articles or filaments, improvement of dimensional precision, improvement of gloss, and prevention of sink.<sup>43</sup>

## a) Nucleation of poly(hydroxybutyrate)

PHB, in addition to being biodegradable and biocompatible, is attractive due to its availability, processibility, and mechanical and barrier properties which are comparable to isotactic PP and other synthetic polymers.<sup>95, 96</sup> PHB is also a highly crystalline thermoplastic that can be extruded, injection molded, and spun<sup>97, 98</sup> into fibers without modification of traditional polymer processing equipment. PHB also has a low elongation at break (less than 10 %), an impact strength of 3 J/mm<sup>2</sup>, a high modulus (1.7 GPa) and a fracture stress of 35 MPa.<sup>99</sup> Despite having these desirable characteristics, PHB is not widely applied in the manufacturing industry, primarily due to its narrow processibility window (PHB melts around 180 °C.<sup>92</sup> very close to its thermal degradation temperature), and to its brittleness which is related to its crystallization behavior. A host of researchers has attempted to resolve these processability issues by other hydroxyalkanoates.<sup>91, 100,</sup> 101 co-polymerizing PHB with mainly hydroxyvalerate and hydroxyhexanoate, blending with poly(ethylene oxide), PVA, or poly(lactide) for example, 102-105, 106, 107 adding plasticizers like citric esters, 108 and processing aids,<sup>109</sup> and/or through annealing.<sup>110</sup>

The crystallographic structure of PHB was elucidated in the early  $1970s^{111,112}$ PHB crystallizes in an orthorhombic system as  $2_1$  chains aligned in groups within an amorphous mass. The lattice parameters are a = 5.76, b = 13.20 and c = 5.96Å, with c corresponding to the fiber period,

R = 0.13. The chains are stacked in well-aligned rows giving two-dimensional order, but the polymer is ill defined along the third axis<sup>113</sup>. Gazzano et al.<sup>114</sup> reported the XRD diffraction patterns for PHB powder, as well as for PHB isothermally crystallized at different temperatures. The changes with varying the crystallization temperature were attributed to strong orientation effects associated with the morphological variations induced by different temperatures. The lattice parameters were not found to change significantly, but the size of the spherulites formed at different  $T_c$  varied.

PHB crystallizes forming large banded spherulites, the structure of which has largely been investigated. The most recent article, published by Tanaka et al.<sup>115</sup> in 2005, gives more insight on the structure of the banded spherulites.

The brittleness of PHB<sup>109,116,117,118,119</sup> is known to stem from three factors: a glass transition temperature close to room temperature, secondary crystallization occurring upon storage at room temperature, and extremely low nucleation density. All these factors are interrelated, and derive from the high purity of PHB and its stereochemical regularity.<sup>50,116</sup> Detailed studies of the crystallization phenomena occurring in bacterial PHB<sup>120,</sup> outline the importance of physical aging as an intrinsic property of this polymer, attributed to progressive crystallization occurring upon storage at room temperature. As a result of its biosynthetic preparation, solvent-based extraction and purification processes, PHB is exceptionally pure and has a very low level of heterogeneous nuclei that could initiate crystallization.<sup>118</sup> Due to its low nucleation density, when cooled from the melt state, PHB forms large spherulitic structures that continue growing

into each other during storage, and are prone to cracking, resulting in materials with low impact resistance and high brittleness.

There is an ongoing research thrust to discover efficient nucleating agents for PHB and its copolymers. Efficient nucleating agents would increase the polymer's crystallization temperature, increase the crystallization rates, and generate smaller and more numerous spherulites, leading to materials with increased mechanical properties. Compounds ranging from talc,<sup>121,122,123</sup> boron nitride,<sup>122,123,40</sup> terbium oxide,<sup>123</sup> lanthanum oxide,<sup>123</sup> saccharin.<sup>40,41</sup> phtalimide.<sup>40</sup> cvclodextrin,<sup>121</sup> and lignin,<sup>124</sup> were investigated as possible nucleating agents for PHB and several nucleation mechanisms were proposed.<sup>122,41,124,118</sup> Among the nucleating agents mentioned above, micro- and nanosize inorganic particles were shown to have the added advantage of acting as reinforcements for the polymer. For example, OMLS nanoplatelets, commonly used as reinforcements for thermoplastic polymers,<sup>125,126</sup> were proven to efficiently nucleate and to reinforce PHB<sup>36</sup> and poly(3-hydroxybutyrate-co-3-hydroxyvalerate).<sup>109</sup> Also. single-walled carbon nanotubes were shown to nucleate PP<sup>80</sup> and to affect the morphology of poly(hydroxybutyrate-cothermal properties and the hydroxyvalerate).81

However, what is apparent from all these studies is that the choice of nucleating agent should be based upon an understanding of the mechanism by which nucleation occurs. Barham<sup>118</sup> summarized the different types of nucleating agents as follows:

*Type A: nucleation from the pure melt*: This is a slow nucleation which occurs when PHB is cooled from a melt or above ~210  $^{\circ}$ C, and does not occur at predetermined sites.

*Type B: self-seeding*: This occurs when PHB is heated no more than ~5 °C above its melting point; there is a higher nucleation density for lower superheatings, and no increased nucleation density if the melt temperature exceeds 205 °C or if the superheating exceeds 200 °C. In addition, the nucleation is reduced if the melt is held at high temperature for more than a few minutes.

*Type C: enhanced self-nucleation*: This is an extension of self-seeding. When the samples are heated to a temperature exceeding the melting point with maximum 1 °C, and then cooled to a crystallization temperature, spherulites simply reappear, as a reverse of melting, not by the usual radial growth process.

Type D: nucleation by impurities: For example, talc (5  $\mu$ m) may act as an impurity and stabilize the self-seeding type of nucleation. The authors of this classification of nucleation mechanisms for PHB specified that if the impurity is added directly to the melt, it will have no nucleating effect; it is only after crystallization of PHB once occurred around the talc that the talc acted as nucleating agent after subsequent melting.

*Type E: "classical nucleation"*: Nucleation by saccharin (particle diameter approximately 50 μm) shows this type of behavior, and occurs both when the agent is added directly to the melt, and when the polymer is first allowed to crystallize around it. Nucleation occurs preferentially on certain faces; it starts on 111 faces, above which the oxygen atoms project; oxygen atoms are spread

approximately 1.185 nm apart. PHB has an axial repeat of ~0.596 nm and fits with little distortion on the saccharin surface.

Barham<sup>117, 118</sup> also proposed a theoretical interpretation of the nucleation rate data collected. The work required for forming a nucleus, in terms of surface free energies and the bulk free energy of fusion, as a function of crystal dimensions,

was calculated. The rate of nucleation is proportional to  $\exp\left(-\frac{\Delta \phi^*}{kT}\right)$ , where

 $\Delta \phi^*$  is the work to form the critical nucleus which, for homogeneous nucleation is given by Equation 1.4.

$$\Delta \phi^{\star} = \frac{32\sigma^2 \sigma_{\theta}}{(\Delta G_V)^2}, \qquad (1.4)$$

where  $\sigma$  is the side surface energy,  $\sigma_e$  is the end, or fold, surface free energy, and  $\Delta G_V$  is the bulk free energy of fusion. The shape of the nucleus was assumed to be a rectangular parallelepiped. For the heterogeneous nucleation on a foreign surface, all the three dimensions of the nucleus are allowed to change. In this case, the work required to form a critical nucleus given by Equation 1.5.

$$\Delta \phi^* = \frac{16\sigma^2 \sigma_{\theta} \Delta \sigma}{(\Delta G_V)^2}, \qquad (1.5)$$

where  $\Delta \sigma = \sigma + \sigma_{os} - \sigma_s$ ,  $\sigma_s$  is the interfacial energy between the foreign surface and the polymer melt, and  $\sigma_{os}$  is the interfacial energy between the

polymer crystal and the foreign surface. In the absence of a substrate,  $\sigma_s = 0$ and  $\sigma_{os} = \sigma$ , hence  $\Delta \sigma = 2\sigma$ . The authors outlined that it was important for the foreign surface to resemble the crystal surface;  $\sigma_s$  is closer to  $\sigma$ ;  $\sigma_{os}$  is closer to zero, and  $\Delta \sigma$  is smaller. The extreme case is obtained when the crystal is identical to the foreign surface, and  $\Delta \sigma = 0$ . Then the work is then:

$$\Delta \phi^* = \frac{4b\sigma\sigma_{\theta}}{\Delta G_V},\tag{1.6}$$

where b is the lattice spacing normal to the surface. The bulk free energy of fusion is:

$$\Delta G_V = \Delta H - T \Delta S . \tag{1.7}$$

At  $T = T_M^0$  (equilibrium melting point),  $\Delta G_V = 0$ , so:

$$\Delta G_V = -\frac{\Delta H \Delta T}{T_M^0}, \qquad (1.8)$$

where  $\Delta H$  is the enthalpy of fusion, and  $\Delta T$  is the supercooling.

A different behavior was observed for the PHB/talc systems, in which the PHB molecules either formed a crystalline layer around the talc, which prevented the polymer from melting, leaving a polymer crystal substrate for subsequent nucleation, or the PHB molecules were partially absorbed onto the talc particles, which reduced their entropy in the molten state. The nucleating effect of saccharin was explained by the absorption of molecules onto the surface in what is close to their crystallographic form.

Another study reported by the Barham<sup>117</sup> refers to the crystallization and morphology PHB. The main purpose of the study was to introduce PHB as a model polymer for studies of morphology and crystallization, and to determine the heat of fusion, surface free energies, and other constants important for further kinetics studies. The effect of seeding on the crystallization of poly(hydroxybutyrate), and co-poly(hydroxybutyrate-co-valerate) was also explored by Withey et al.<sup>40</sup> The enhanced self-seeding of PHB upon addition of PHB crystals was also investigated. Additionally, mixtures of PHB with saccharin and phtalimide were studied in the view of explaining the nucleating effects. The development of crystallinity within the mixtures, and the relative ability, and the relative ability of the nucleating agents to induce crystallization of PHB/PHBV were studied. Samples were prepared by compression molding, and analyzed using polarized optical microscopy (with a hot stage). SEM imaging of the fracture surfaces, FT-IR, and DSC. Boron nitride was found to nucleate better than saccharin and phtalimide. Phtalimide had almost no nucleating ability, and both saccharin and phtalimide appeared to be soluble in the melt but were less soluble in the crystalline regions. These findings are unique since FT-IR was used for microstructural analysis, in order to establish local compositions within the boundaries of the spherulites. It was pointed out that saccharin and phtalimide were excluded from the growing polymer crystallites and accumulated at the interface between the spherulites boundary and the melt. The conclusion

was that the mixtures formed a complex-phase system with both saccharin and phtalimide being present at the intersection of polymer spherulites.

Recently, Kai et al.<sup>122</sup> reported a closer look at the fast crystallization of poly(3-hydroxybutyrate) and poly(3-hydroxybutyrate-co-3-hydroxyvalerate) with talc and boron nitride as nucleating agents. Two nucleation mechanisms were proposed for boron nitride and talc.

### b) Nucleation of polylactic acid

The crystallization rates of various types of poly(lactic acid) are very slow as compared with commercially useful thermoplastics such as polyethylene, and it has been established that there is a clear need to use nucleating agents to modify this polymer's crystallization behavior. The traditional approach of employing heterogeneous nucleating agents in order to reduce process cycle times, increase the crystallization temperature, and diminish the size of crystallites, was investigated for PLA by numerous authors.<sup>127,128</sup>

As pointed out by Schmidt et al. <sup>128</sup>, without the addition of nucleating agent, the half-time of crystallization ( $t_{1/2}$ ) is very high, 1.9 minutes for a PPLA sample with a molecular weight of ~100 kg/mol. For a similar PLLA sample<sup>127</sup>, 6 wt % talc, a common nucleating agent for semicrystalline polymers, was found to increase the crystallization rate of PLLA. In this case,  $t_{1/2}$  was less than one minute at crystallization temperatures between 90 °C and 120 °C.

Organically modified layered silicate nanocomposites (OMLS) of PLA were first reported in 1997 by Ogata et al<sup>37</sup>. The PLA/OMLS were prepared by

dissolving the PLA in hot chloroform in the presence of a modified montmorillonite (MMT), and showed an increase in Young's modulus as compared to the neat PLA. In this very first study, the layered silicates were shown to act as nucleating agents for PLA. Figure 1.9 shows the DSC thermograms of PLLA/OMLS blends<sup>37</sup>. The exothermic peaks in the temperature region between the glass transition temperature and the melting temperature correspond to cold crystallization. The peaks are narrower for PLA/OMLS blends than for PLA, and the fact that the peak temperatures are lower for PLA containing OMLS than for the neat PLA suggests that the small OMLS particles act as nucleating agents.



Figure 1.9 DSC curves of quenched PLLA/OMLS blends containing different amounts of OMLS

Extensive research was being conducted on PLA/layered silicates nanocomposites by the Okamoto group at the Toyota Technological Institute in Japan. The same nucleating effect was observed in nanocomposites obtained from organically modified synthetic fluorine mica (OMSFM)<sup>129</sup>. Figure 1.10<sup>130</sup> shows the DSC curves obtained during heating of PLA, and PLA containing 4 wt % OMSFM, and the polarized optical micrographs obtained for the same samples. The neat PLA crystallized at 110 °C had a well-defined, large spherulitic morphology, while the size of the spherulites decreased upon the addition of the OMSFM, which evidently increased the number of nuclei and modified PLA's crystallization behavior.

The same group reported on the effect of layered silicates on the crystallization kinetics of PLA<sup>131,132</sup>, underlining the importance of knowing the crystallization of PLA in detail, and how it is affected by the presence of OMLS nanoplatelets. In their first study of the crystallization behavior of PLA/clay systems, crystallization kinetics of nanocomposites obtained from PLA and octadecylammonium modified montmorillonite prepared by extrusion was investigated using time-resolved LS photometry. The dependence of the overall crystallization rate (Figure 2.10), and of the diameter of PLA spherulites on the crystallization rate was rigorously quantified. The kinetic analysis, together with a polarized optical microscopy study, revealed that the dispersed clay particles acted as nucleating agents for PLA.



Figure 1.10 DSC traces of neat PLA and PLA/CN. (b) Polarized optical micrographs of crystallized (at 110 °C) samples of neat PLA and PLA/CN

Moreover, for PLA and PLA/OMLS, the group reported on the dependence of the spherulite radius, and of the overall crystallization rate on the crystallization temperature<sup>131</sup> (Figure 1.11), as well as on the relationship between the nucleation density and the crystallization temperature.



Figure 1.11 Dependence of the overall crystallization rate of PLA, and PLA/OMLS nanocomposites on the crystallization temperature

A subsequent study compared five different organically modified layered silicates in terms of their effects on the crystallization of PLA. The conclusion was that the surface of OMLS acts as nucleating agent, increasing the crystallization temperature, and affecting the morphology of the resulted nanocomposites. The PLA/OMLS systems were proven to undergo heterogeneous nucleation kinetics. An important observation regarding morphology was that the spherulites of PLA/OMLS had a less ordered structure than those of pure PLA, due to the OMLS particles that were not nucleating and were dispersed in the spherulites, disturbing the regular orientation of the lamella stacks inside the spherulites.<sup>131</sup>

### Exfoliated graphite nanoplatelets as nucleating agents

The structure of graphite is very similar to the one of boron nitride (Figure 1.12), which was previously shown to act as efficient nucleating agent for PHB. xGnP were also shown to act as nucleating agents<sup>133</sup> and reinforcement for other thermoplastic polymers<sup>133;30;29</sup>, and have a series of extremely structure-related attractive advantages.



Figure 1.12 Boron nitride crystal structures

Graphite is a layered natural mineral, and the layers can be intercalated and exfoliated into nanosize platelets with high aspect ratio, high surface area and in-plane stiffness as high as 1060 GPa.<sup>134</sup> While the basal plane is inert (consisting of carbon in its sp2 state along with a graphene surface rich in  $\pi$  electrons), the existence of functional groups (Figure 1.13) at the edges can lead to hydrogen or covalent bond with polymer matrices. However, it should be noted that with the typical large aspect ratios of xGnP (~100) the amount of edge sites compared to basal plane sites is very small.



Figure 1.13 Schematic of the xGnP

Exfoliated graphite nanoplatelets having an average size of 1  $\mu$ m (xGnP-1) were produced in-house<sup>26, 135</sup> starting from GrafGard<sup>TM</sup> 160-50A acid intercalated graphite produced by Graftech (Cleveland, OH). The xGnP prepared with our MSU method has a surface area of approximately 100 m<sup>2</sup>/g and consists of platelets approximately 10 nm in thickness and 1  $\mu$ m in diameter. The platelet basal plane is a graphene sheet, uniform in structure and surface energy, with evidence of some oxygen functionalities located at the edges of these basal surfaces.

Recent research<sup>133</sup> in the Drzal group showed that the graphene basal plane promotes nucleation of PP. At low xGnP concentration, PP was shown to crystallize in a less common  $\beta$ -form, consisting in crystals with higher impact strength. Besides the concentration of xGnP, crystallization conditions were also shown to affect the population and size of PP spherulites, which clearly

influenced the electrical conductivity of the resulted PP/xGnP nanocomposites. The PP/xGnP study indicates that smaller and more numerous crystallites formed by PP in the presence of xGnP may disrupt the formation of conductive network, thus increasing the percolation threshold for electrical conductivity. This research strongly indicates that in order to achieve control over nanocomposite properties it is extremely important to understand the effects of xGnP on the crystallization of the polymer matrix in which the nanoplatelets are incorporated.

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#### **CHAPTER 2**

## NUCLEATION OF POLY(HYDROXYBUTYRATE) BY EXFOLIATED GRAPHITE NANOPLATELETS

#### Introduction

PHB is a largely investigated polymer derived from renewable resources which has not yet found extended industrial applications, mainly due to brittleness and a low processability window. The brittleness of PHB<sup>1,2,3,4,5</sup> is known to stem from three factors: a glass transition temperature close to room temperature, secondary crystallization occurring upon storage at room temperature, and extremely low nucleation density. All these factors are interrelated, and derive from the high purity of PHB and its stereochemical regularity.<sup>3</sup>

As described in Chapter 1, boron nitride (BN) is a commonly used efficient nucleating agent for PHB. The structure of graphite is similar to that of BN, and xGnP has the potential to provide a similar nucleating effect on the polymer. Graphite can be intercalated and exfoliated into very thin nanosized platelets<sup>6</sup> with extremely high surface area and in-plane stiffness as high as 1060 GPa<sup>7</sup>, which can not only nucleate PHB, but also impart multifunctionality to the

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polymer and expand the range of its applications. This chapter describes the nucleating effect of xGnP on PHB.<sup>8</sup>

Understanding the nucleating effect of xGnP, specifically the kinetic and morphologic aspects of the nonisothermal crystallization from the melt of PHB and PHB/xGnP systems, is essential for optimizing the processing conditions for thermoplastic materials under dynamic conditions such as extrusion and injection molding.<sup>9,10,11,12</sup> A kinetic analysis of the nonisothermal crystallization from the melt was undertaken using models based on modifications of the Avrami equation. Optical microscopy and atomic force microscopy (AFM) were used to characterize the morphologies of PHB/xGnP systems and to offer further insight on the crystallization process.<sup>13,14,15</sup> AFM was used to study the surface morphology and nanostructure of the PHB/xGnP system offering insights into processes such as crystallization, crystal thickening and crystal deformation, phenomena which were also observed *in situ*.<sup>16</sup>

The study described in this chapter constitutes work published in 2007 in Journal of Applied Polymer Science.<sup>8</sup>

#### **Experimental details**

#### <u>Materials</u>

PHB of 900,000 g/mol number average molecular weight was obtained from Metabolix (Cambridge, MA), and used without further purification. The exfoliated graphite nanoplatelets having an average size of 1  $\mu$ m (xGnP-1) was produced

in-house<sup>6,17</sup> starting with an acid intercalated graphite 160-50A produced by Graftech (Cleveland, OH). The xGnP has a surface area of ~100 m<sup>2</sup>/g and consists of platelets approximately 10 nm in thickness and 1  $\mu$ m in diameter. The platelet basal plane is a graphene sheet, uniform in structure and surface energy with evidence of some oxygen functionalities located at the edges of these basal surfaces.

#### Sample preparation

Samples of pure PHB and PHB containing, 0.01 % wt, 1 % wt, and 3 % wt xGnP-1 were prepared by extrusion and injection molding. The PHB powder, previously dried in a vacuum oven at 80 °C for three hours to remove the moisture, was mixed with the xGnP-1 and extruded using a DSM micro-extruder (15 cm<sup>3</sup> capacity) (DSM Research B.V., The Nederlands). The temperatures in the three heating zones of the micro-extruder were 175 °C, 185 °C, and 195 °C respectively. The mixtures were extruded at 100 rpm, and the cycle time was three minutes. The extruded polymer systems were transferred using a transfer cylinder (kept at 190 °C) to a mini-injection molder and injection molded at a fixed temperature of 50 °C.

#### <u>Methods</u>

#### a) Thermal analysis: differential scanning calorimetry

The melting and crystallization behavior of PHB/xGnP-1 samples were investigated using a 2920 Modulated DSC (TA Instruments). The runs were performed under nitrogen flow, after calibrating the DSC instrument using an

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Indium standard. For each run, a fresh sample (5-10 mg) of polymer was heated from room temperature to 190 °C, kept isothermal for five minutes, in order to remove the thermal history, then cooled to -60 °C, reheated to 190 °C, and cooled to room temperature. The heating/cooling rate was 10 °C/min for the first heating/cooling cycle. Six different heating/cooling rates were used for the second heating/cooling cycle: 5, 8, 10, 14, 17, and 20 °C/minute. The analysis employed the data recorded during the second cooling step. During the nonisothermal crystallization of PHB study, the samples were run consecutively, using the same sealed aluminum pan as control to reduce error.

#### b) Optical microscopy

The samples for optical microscopy were prepared as thin polymer films by heating very thin sections of PHB/xGnP-1 injection molded bars in a Mettler Toledo FP82 hot stage. Specifically, the polymer was placed on glass or mica slides, covered with glass or mica cover slips, and heated at a rate of 20 °C/minute from room temperature to 190 °C, kept isothermal for three minutes, then either allowed to crystallize upon cooling to room temperature, or to crystallize isothermally at different preset crystallization temperatures. The morphology of PHB and the size of the spherulites were observed using an Olympus BH2 optical microscope equipped with a Spot™ camera.

#### c) Atomic force microscopy

Thin polymer films were prepared as described for optical microscopy, using the Mettler Toledo FP80 hot stage. All images were collected on a Nanoscope<sup>TM</sup> IV instrument (Veeco, Santa Barbara, CA) equipped with a J scanner. Images were collected in either contact or tapping mode, using commercially available silicon or silicon nitride cantilevers. The AFM was initially calibrated by the manufacturer but because of the nonlinear electrical response of piezo materials, the electrical signals applied to SPM scanners were periodically calibrated to ensure accuracy. Calibration standards, e.g. the TGZ01 standard (MikroMasch, CA) were imaged to ensure that the pitch and z distances are in agreement with those specified by the manufacturer. Images were typically collected at a scan rate of 0.5 Hz for scans sizes larger than 5×5  $\mu$ m and up to 1 Hz for scan sizes less than 1×1  $\mu$ m. Some of the images were first-order flattened and scan lines were erased.

#### d) Wide angle X-ray diffraction

X-ray diffraction traces of extruded and injection molded PHB/xGnP samples were measured at room temperature in the scattering angle range  $5^{\circ} \le 2\theta \le 45^{\circ}$  by using a Rigaku 200B X-ray imaging plate diffractometer equipped with a curved graphite monochromator. The scanning rate was 0.020 °/s. Cu K $\alpha$  radiation (wavelength 1.5418 Å) from a Rigaku rotating anode X-ray generator was used as an incident X-ray source (50 kV, 100 mA).

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#### **Results and discussion**

#### Crystallization of PHB in the presence of xGnP-1

The nonisothermal crystallization of pure PHB and PHB containing 1 % wt, and 3 % wt xGnP-1 from the melt was studied using differential scanning calorimetry. The melting temperature ( $T_m$ ), the onset and end of crystallization temperatures ( $T_0$  and  $T_\infty$ ), the temperature of the crystallization peak ( $T_p$ ), the enthalpies of fusion and the crystallization enthalpies ( $\Delta H_f$  and  $\Delta \underline{H}_c$ ) were recorded for heating/cooling at six different rates (5, 8, 10, 14, 17, and 20 °C/minute respectively). Figure 2.1 shows the nonisothermal crystallization curves for the PHB/xGnP-1 systems described above. After the addition of xGnP-1, the crystallization peaks shifted to higher temperatures, which was the first indication of the nucleating effect of xGnP-1.



Figure 2.1 Nonisothermal crystallization curves obtained for (a) pure PHB, (b) PHB/1% xGnP-1 and (c) PHB/3% xGnP-1 at six cooling rates: 5°C/min; 8°C/min; 10°C/min; 14°C/min; 17°C/min; and 20°C/min respectively. (The arrows indicate increasing cooling rates.)

The crystallization peaks also became narrower, which suggested that PHB spherulites formed in the presence of xGnP-1 were smaller than the spherulites formed by the neat polymer. Figure 2.2,a and Table 2.1 summarize the values of  $T_p$  recorded for PHB containing different concentrations of xGnP-1, at different cooling rates. Figure 2.2,b and Table 2.1 show that for PHB/xGnP-1 systems, the degrees of supercooling (defined as the difference between the melting

temperature and the temperature of the crystallization peak,  $\Delta T = T_m - T_p$ ) were lower than that of pure PHB. The nucleating effect of graphite nanoplatelets was more evident at lower concentrations. Both the shifts of the crystallization peaks and the decreases of the degree of supercooling are evidence of the nucleating effect of xGnP-1.



Figure 2.2 Graphs showing (a) the temperature of crystallization peaks and (b) the degrees of supercooling versus cooling rate for pure PHB (■), PHB/0.01% xGnP-1 (o), PHB/1% xGnP-1 (•), and PHB/3% xGnP-1 (▲).

	Zc		0.1317	0.0633	0.0845	0.2455	0.3470	0.7153		Z,		0.9556	0.9521	0.9806	0.9880	0.9913	0.9929		Z		0.9472	0.9725	0.9782	0.9877	0.9902	0.9924			
	log(-Z <sub>c</sub> )		-2.0274	-2.7592	-2.4705	-1.4044	-1.0584	-0.3350					log(-Z_)	5	-0.0454	-0.0491	-0.0195	-0.0120	-0.0088	-0.0071		log(-Z <sub>c</sub> )		-0.0543	-0.0279	-0.0221	-0.0124	-0.0098	-0.0076
	Z							-6.7006		Z		-0.2271	-0.3927	-0.1955	-0.1686	-0.1488	-0.1420		Z		-0.2714	-0.2232	-0.2208	-0.1733	-0.1671	-0.1520			
	(Z-)gol		2.3162	3.0944	3.2070	2.9787	2.8900	1.9022		log(-Z)		-1.4825	-0.9347	-1.6324	-1.7802	-1.9053	-1.9518		(Z-)bol	5	-1.3043	-1.4995	-1.5104	-1.7528	-1.7894	-1.8840			
	u		1.8539	2.3035	2.3837	2.0240	1.9675	2.8361		u		0.4208	0.3856	0.3471	0.4119	0.3946	0.4184		u		0.3698	0.4291	0.3948	0.4443	0.5130	0.5732			
	t112	[min]	3.33	2.55	2.48	1.78	1.55	1.49	SnP-1	t112	[s]	1.85	1.58	1.24	0.9	0.73	0.6	SnP-1	t112	[min]	2.77	1.95	1.8	1.07	0.99	0.81			
PHB	t <sub>max</sub>	[min]	6.89	5.24	4.41	3.22	2.91	2.72	HB+1%x0	tmax	[min]	4.70	3.90	3.19	2.52	1.58	1.72	HB+3%xC	tmax	[min]	5.68	3.54	3.49	2.10	1.76	1.43			
	$\Delta T$	[်င]	81.30	87.51	90.39	95.38	99.47	107.12	ď	$\Delta T$	[c]	45.47	59.76	58.13	53.63	62.36	61.48	d.	$\Delta T$	ြှ	52.47	59.96	20	64	70.27	70.63			
	$T_m$	[c]	174.44	174.15	173.80	173.42	174.42	173.33		Tm	[,c]	161.6	167.8	162.3	160.02	162	161.64		Tm	[,c]	168.6	168	174.17	170.39	169.91	170.79			
	T.,	[c]	74.35	63.26	62.64	56.47	51.07	47.99		T.,	[c]	105	66	96	88	06	88		T.	[c]	100.07	93.116	84.628	89.468	84.209	83.936			
	Tp	[c]	93.14	86.64	83.41	78.04	74.95	66.21		Tp	[c]	116.13	108.04	104.17	106.39	99.64	100.16		Tp	[c]	116.13	108.04	104.17	106.39	99.64	100.16			
	T <sub>0</sub>	[c]	109.00	105.47	106.99	101.88	100.84	101.33		To	[°C]	129	127	128	124	121	123		To	ြှ	128.66	121.63	119.99	119.07	114.37	112.73			
	D	[°C/min]	5	80	10	14	17	20		D	[°C/min]	5	8	10	14	17	20		D	[°C/min]	2	80	10	14	17	20			

 Table 2.1
 Summary of modified Avrami analysis results

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#### Kinetic analysis of the nonisothermal crystallization from melt

Based on the shifts of  $T_{p}$ , the narrowing of the crystallization peaks, and the decrease of the degree of supercooling of PHB after the addition of xGnP-1, it was concluded that maximum crystallinity of PHB crystallizes was achieved faster in the presence of xGnP-1. In order to verify this, a kinetic analysis was performed to compare the nonisothermal crystallization from the melt of the various PHB/xGnP-1 systems. Most methods used for describing nonisothermal crystallization are based on modifications of Avrami equation (Equation 2.1),<sup>18,10,11,12,19,20,21,22</sup> which accurately describes isothermal crystallization of polymers:

$$1 - X_t = \exp(-Zt^n), \qquad (2.1)$$

where  $X_t$  is the relative degree of crystallinity, *Z* is an overall rate constant characterizing both nucleation and growth contributions, and *n* is a mechanism constant whose value depends on the type of nucleation and growth process parameters.<sup>11</sup> A modification proposed by Jeziorny,<sup>22</sup> and applied to PHB,<sup>9</sup> successfully described the kinetics of nonisothermal crystallization of PHB/xGnP-1 samples. The cooling rate (*D*), assumed to be constant, was the factor used in correcting the rate constant, *Z*, as shown in Equation 2.2. The relative degree of crystallinity,  $X_t$ , and the absolute degree of crystallinity at each crystallization temperature,  $X_c$ , were determined using (Equations 2.3 and 2.4).

$$\log Z_c = \frac{\log Z}{D} \tag{2.2}$$

$$X_{c} = \frac{\int_{\tau_{0}}^{T} \left(\frac{\mathrm{d}Hc}{\mathrm{d}T}\right) \mathrm{d}T}{(1 - w_{xGnP-1}) \cdot \Delta H_{f}^{0}}, \qquad (2.3)$$

$$X_{t} = \frac{\int_{T_{0}}^{T} \left(\frac{\mathrm{d}Hc}{\mathrm{d}T}\right) \mathrm{d}T}{\int_{T_{0}}^{T_{\infty}} \left(\frac{\mathrm{d}Hc}{\mathrm{d}T}\right) \mathrm{d}T},$$
(2.4)

where  $w_{xGnP-1}$  is the mass fraction of xGnP-1 in the polymer system,  $\Delta H_f^0 = 146 \text{ J/g}$  is the thermodynamic melting enthalpy of 100 % pure crystalline PHB,<sup>23</sup> and  $\Delta H_c$  is the crystallization enthalpy recorded by DSC.

The development of relative crystallinity with temperature for the PHB/xGnP-1 systems investigated is presented in Figure 2.3.

In each of the three cases, after adding xGnP-1 to PHB, complete crystallization was achieved over a narrower temperature range (Figure 2.3), and also in a shorter time Table 2.1.



Figure 2.3 Development of relative crystallinity with temperature for (a) pure PHB, (b) PHB/1% xGnP-1, (c) PHB/3% xGnP-1 at six cooling rates: 5°C/min; 8°C/min; 10°C/min; 14°C/min; 17°C/min; and 20°C/min, respectively. (The arrows indicate increasing cooling rates.)



Figure 2.4 Development of relative crystallinity with time for (a) pure PHB, (b) PHB/1% xCnP-1, (c) PHB/3% xCnP-1 at six cooling rates: 5°C/min; 8°C/min; 10°C/min; 14°C/min; 17°C/min; and 20°C/min respectively (The arrows indicate increasing cooling rates.) The S-shaped curves indicate that pure PHB crystallizes in two steps, and this phenomenon, also observed for ethylene terephtalate-ethylene oxide segmented copolymers,<sup>11</sup> is explained in terms of an initial fast growth phase of the crystals in an amorphous environment, followed by a slower growth phase as the crystals begin to impinge on each other in the interlamellar region.

The kinetic parameters for the nonisothermal crystallization PHB/xGnP-1 samples were determined by plotting  $\log[-\ln(1-X_t)]$  versus  $\log t$  (Figure 2.5).



**Figure 2.5** Graphs showing the results of modified Avrami analysis for (a) PHB, (b) PHB/1% xGnP-1, and (c) PHB/3% xGnP-1 at six cooling rates

For pure PHB, and PHB containing 1 % wt and 3 % wt xGnP-1, the curves were linear at first and then deviated from linearity, due to secondary crystallization.<sup>10</sup> However, for systems containing 0.01 % wt xGnP-1, the plots were not linear, possibly due to non-uniform dispersion of xGnP-1 in PHB, a result of poor mixing in the micro-extruder. Hence, these samples were not further subjected to kinetic analysis. The values of the kinetic parameters *n*, *Z*, and *Z*<sub>c</sub> for neat PHB, and for PHB containing 1 % wt and 3 % wt xGnP-1 were obtained from the slopes and intercepts of the lines Figure 2.5, and are summarizedin Table 2.1. According to the modified Avrami analysis, the rate of crystallization of pure PHB increased with increasing cooling rate (Figure 2.6).



# Figure 2.6 Nonisothermal crystallization rate parameters for PHB/xGn-1 systems, determined according to modified Avrami analysis

For PHB samples containing 1 % wt and 3 % wt xGnP-1, the kinetic parameters of the crystallization process were higher than for pure PHB, but were independent of the cooling rate. Our results furthermore show that the time

required to achieve half of the final crystallinity ( $t_{1/2}$ ), as well as the maximum crystallization time, were higher for pure PHB than for PHB containing exfoliated graphite nanoplatelets (Figure 2.7,a, b, and Table 2.1.



Figure 2.7 Graphs showing (a) the half-time crystallization times and (b) the maximum crystallization times for pure PHB (■), PHB/0.01% xGnP-1 (o), PHB/1% xGnP-1 (•), and PHB/3% xGnP-1 (▲), determined according to modified Avrami analysis

The activation energies for the nonisothermal crystallization from melt were determined using the Kissinger method,<sup>10,24</sup> (Equation 2.5) based on the peak temperatures recorded by DSC for different cooling rates (Table 1):

$$\frac{d\left(\ln\left(\frac{D}{T_{\rho}}\right)\right)}{d\left(\frac{1}{T_{\rho}}\right)} = -\frac{\Delta E}{R},$$
(2.5)

where R is the universal gas constant,  $\Delta E$  is the activation energy, and the other parameters are as defined previously. The activation energies were calculated

using the slopes of the lines obtained by plotting  $\log\left(\frac{D}{T_p^2}\right)$  vs  $\frac{1}{T_p}$  (Figure 2.8, and

Table 2.1).

For PHB, PHB/ 1 % wt xGnP-1, and PHB/ 3 % wt xGnP-1, the activation energies were found to be -60.41 kJ/mol, -213.61 kJ/mol, and -101.86 kJ/mol respectively (Figure 2.9).  $\Delta E$  for the nonisothermal crystallization from melt of PHB was in agreement with the value of -64.6 kJ/mol reported by An *et al.*<sup>9</sup>



**Figure 2.8** Kissinger plots used for determining the activation energy for nonisothermal crystallization of pure PHB (■), PHB/0.01% xGnP-1 (o), PHB/1% xGnP-1 (•), and PHB/3% xGnP-1 (▲)



Figure 2.9 Activation energies for the nonisothermal crystallization from melt of PHB/xGnP-1 systems

#### Morphology of PHB/xGnP-1 composites

Optical microscopy was used to observe the distribution and growth of the crystallites formed by pure PHB and PHB/xGnP-1 systems during nonisothermal cooling from the melt, and their morphologies after crystallization. As shown in Figure 2.10,a, pure PHB formed large, well-defined banded spherulitic structures having an average radius of 70 µm.

The optical micrographs obtained for PHB/1 % wt xGnP-1 and PHB/3 % wt xGnP-1 (not shown) showed agglomerations of numerous, small spherulites which crystallized spontaneously from the melt. This result was not unexpected since the high concentration of xGnP-1 added (1 and 3% wt) introduced many heterogeneous nuclei which initiated nucleation of the PHB at 110-113 °C. In an attempt to observe the crystallization of PHB in the presence of xGnP-1, PHB samples containing 0.01 % wt xGnP-1 were prepared. The addition of a lower

concentration of xGnP-1 to PHB led to the formation of spherulites now large enough to be observed with optical microscopy (Figure 2.10,b).



Figure 2.10 Optical micrographs showing spherulites of (a) pure PHB and (b) PHB/0.01 wt % xGnP-1 formed during nonisothermal crystallization from the melt.

AFM was employed to provide further details regarding the sizes of the spherulites and topographical information. AFM images were collected for the pure PHB, and PHB containing 0.01 % wt, 1 % wt and 3 % wt xGnP-1 (Figure 2.11). Figure 2.11,a shows an AFM height image of a PHB spherulite formed upon nonisothermal crystallization of PHB from the melt, having an approximate diameter of 90 µm, which is most likely an overestimation due to tip

convolution effects. Figure 2.11,b shows an AFM height image for a spherulite formed from the PHB/0.01 % wt xGnP-1 system also having a diameter of about 90  $\mu$ m. In the case of the PHB/xGnP-1 systems having higher concentrations of graphite nanoplatelets, the crystallites formed appeared to be much smaller and impinged into each other (Figure 2.11,b,c), so despite the accuracy of AFM, due to the nature of the sample, it was difficult to determine the exact sizes of the spherulites.



Figure 2.11 AFM tapping mode height images (top view) showing spherulites of (a) pure PHB and PHB containing, (b) 0.01 wt % xGnP-1, (c) 1 wt % xGnP-1 and (d) 3 wt % xGnP-1

These AFM results indicate that the lamellar thickness of pure PHB spherulites crystallized from the melt ranges from 7 to 20 nm, as shown in the cross-sectional analysis in Figure 2.12.a.



Figure 2.12 AFM tapping mode height images (top view) and accompanying cross-sections showing the lamellar thicknesses of spherulites of (a) pure PHB and (b) PHB/1 % wt xGnP.

The lamellar structure was also observable in the PHB/1 % wt xGnP-1 system at small scan sizes (250×250 nm) (Figure 2.12,b), and the thickness was measured to be approximately 5 nm. On the other hand, AFM images of PHB/3 % wt xGnP-1 samples revealed an apparent disruption of the lamellar structure, attributed to the wide distribution of xGnP-1 throughout the crystalline structure (Figure 2.13).



Figure 2.13 AFM height image (top view) of PHB/3 % xGnP-1 showing the apparent disruption of the lamellar structure of the polymer

Overall, these results indicate that the lamellar thickness decreased as the amount of xGnP-1 increased, and was proportional to the size of the crystalline structures formed.

These experimental results are consistent with theoretical values for lamellar thicknesses, calculated using Equation 2.6, which relates lamellar thickness to the equilibrium melting temperature of polymers<sup>4</sup>:

$$T_m = T_m^0 \left( 1 - \frac{2\sigma_\theta}{\Delta H I} \right), \tag{2.6}$$

where  $T_m$  is the observed melting point,  $\sigma_e$  is the fold surface free energy,  $\Delta H$  is the heat of fusion, and / is the lamellar thickness. Using this correlation and the values reported for  $\sigma_e$  and  $\Delta H$  ( $38 \pm 6 \times 10^{-3}$  J/m<sup>2</sup> and  $1.85 \times 10^8$  J/m<sup>3</sup> respectively,<sup>4</sup> the lamellar thickness, was estimated to be in the range of 17 to 24 nm. Since the addition of xGnP-1 greatly increases the heterogeneous nucleation ability of PHB, and hence the fold surface energy of the PHB/xGnP-1 composite is expected to differ from pure PHB, the theoretical estimation was not applied for PHB/xGnP-1 systems.

AFM was also employed by Skyes et al.<sup>25</sup> and Murase and coworkers,<sup>26</sup> who used this technique to investigate solution-grown PHB single crystals prepared from bacterial PHB by alkali hydrolysis, and reported the lamellar thickness to be approximately 5 nm.

WAXD measurements lead to the hypothesis of epitaxial growth of PHB onto xGnP-1 surfaces. Figure 2.13 shows WAXD results obtained for PHB nanocomposites containing various amounts of xGnP-1. For increasing amounts of graphite, the relative intensity of the 020 and 110 diffraction peaks of PHB is inverted, corresponding to a preferential growth of the crystals on the xGnP basal plane. The intensity of the amorphous peaks recorded around  $2\theta = 22$  ° decreases as the amount of xGnP-1 in PHB increases, which is in agreement with previously reported DCS measurements of the crystallinity of PHB/xGnP-1 nanocomposites.



Figure 2.14 Summary of WAXD analysis of PHB/xGnP-1 nanocomposites

This thermal behavior is particularly desirable for dynamic processing conditions such as extrusion and injection molding, which are largely utilized for obtaining biocomposites. The effects of xGnP on the crystallization behavior and morphology of PHB provides a foundation for additional investigations of the PHB/xGnP systems with controllable thermal and mechanical properties, and electrical conductivity.

#### Conclusions

This research has shown that exfoliated graphite nanoplatelets efficiently nucleate PHB, leading to systems that crystallize from the melt faster and at higher temperatures. Very small amounts of xGnP-1 (0.01 % wt) increased the crystallization temperature of PHB by approximately 30 °C, leading to the formation of smaller spherulites, as evidenced by optical microscopy and atomic force microscopy. A modified form of Avrami equation accurately described the nonisothermal crystallization from melt of PHB/xGnP-1 systems, and showed that this process occurred faster for PHB/xGnP-1 systems than for pure PHB. The pure polymer crystallized faster as the cooling rate increased, while the kinetic parameter describing the nonisothermal crystallization from the melt of rates of the PHB/xGnP-1 systems were almost independent of the cooling rate. Additionally, nonisothermal crystallization from the melt was shown to be more energetically favored for the systems containing xGnP than for pure PHB. Maximum crystallinity was also achieved faster in PHB/xGnP-1 systems than in pure PHB. Although, the kinetic analysis and activation energies indicate that 3 wt % xGnP in PHB is excessive for initiating nucleation, it should be noted that the excess xGnP may act as a nano-reinforcement, thereby leading to enhanced mechanical properties and possibly achieving electrical conductivity in the bionanocomposites through percolation of the xGnP network.

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#### **CHAPTER 3**

## MODIFICATION OF CRYSTALLINITY AND xGnP/PHB INTERACTION WITH IONIC LIQUIDS IN PHB/xGnP NANOCOMPOSITES

This chapter describes the potential use of ionic liquids in PHB/xGnP nanocomposites, with a dual role of plasticizing the polymer matrix, and possibly controlling the nucleating effect of xGnP.

#### Introduction

lonic liquids (ILs) are a new class of environmentally friendly compounds. They are classified as salts which melt at temperatures around 100°C, and have an appreciable liquid range. Some of these compounds have melting points around room temperature and are termed Room Temperature lonic Liquids (RTIL). ILs are sometimes defined "organic" salts because their structures are based on big organic cations. The most common cations and anions are represented<sup>3</sup> in Table 3.1. The degree and type of substitution of these bulky asymmetric cations determines the low melting points of these salts, due to a reduction of Coulombic interactions and disruption in the ion-packing and reduction of the lattice energy. The anions control the compounds' interaction with water, the coordinating ability, and the hydrophobicity.

Besides the remarkably low melting points, ILs have no measurable vapor pressure, are not flammable, and not oxidizing. Most of the applications of ILs are related to their good solvent abilities, as these salts were proved to be good solvents for a large range of organic and inorganic compounds. ILs fit very well into the frame of green chemistry and are part of the general effort to reduce the emission of volatile organic compounds.

The brittleness of PHB, which has a glass transition temperature close to room temperature, is commonly addressed by addition of plasticizers. ILs were shown to plasticize semicrystalline polymers such as PVC<sup>28</sup> and PMMA<sup>1, 2</sup>, which indicates their potential to act as plasticizers for PHB. Since the mechanical properties of PHB depend to a large extent on the crystallinity, and since the presence of xGnP has been shown to have a significant effect on the crystallization temperature, kinetics and crystalline morphology, imidazolium-based ionic liquids (ILs) were investigated for their potential to modify PHB brittleness as well as the interaction between the xGnP and the PHB polymer. The large organic cations in ILs have a tremendous potential to interact with the *pi* electrons on graphitic surfaces (through cation- $\pi$  interactions), leading to the possible use of ILs for surface modification of xGnP. The adsorption of ILs onto xGnP surface was expected to alter the nucleating ability and to offer more control over heterogeneous nucleation processes.

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Table	3.1	Common	cations	and	anions	in	ionic l	iquids
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MOST COMMONLY USED CATIONS:											
R2 N R1	+ N R	$\begin{bmatrix} R1 \\   \\ N \\ R2 \\ R3 \end{bmatrix}$	$\begin{bmatrix} R1 \\   \\ P \\ R2 \\ R3 \end{bmatrix} \oplus$								
1,3-dialkyl-imidazolium	N-alkyl pyridinium	Tetraalkylammonium	Tetraalkylphosphonium								
EXAMPLES OF ANIONS:											
Water insoluble			Water soluble								
[PF <sub>6</sub> ] <sup>-</sup>			[CH <sub>3</sub> CO <sub>2</sub> ] <sup>−</sup>								
[(CF <sub>3</sub> SO2) <sub>2</sub> N] <sup>-</sup>	[BF4]-		[CF <sub>3</sub> CO <sub>2</sub> ], [NO <sub>3</sub> ]-								
[(C <sub>2</sub> F <sub>5</sub> ) <sub>3</sub> PF <sub>3</sub> ] <sup>-</sup>	[CF₃SO₃] <sup>-</sup>		Br <sup>-</sup> , Cl <sup>-</sup> , l <sup>-</sup>								
[BR <sub>1</sub> R <sub>2</sub> R <sub>3</sub> R <sub>4</sub> ] <sup>-</sup>			[Al₂Cl7] <sup>-</sup> , [AlCl₄] <sup>-</sup>								

#### Effects of two imidazolium phosphates on PHB

The potential plasticizing effect of two ionic liquids, 1-ethyl-3methylimidazolium hexafluorophosphate (IL1) and 1-butyl-3-methylimidazolium hexafluorophosphate) (IL2), was evaluated. PHB samples containing IL1 and IL2 were compared with PHB containing triethyl citrate (TEC), a common plasticizer for thermoplastic biobased polymers. The various plasticized PHB systems were compared in terms of mechanical properties (flexural strength and modulus, and impact strength), glass transition temperature, as well as in terms of polymer-plasticizer miscibility. Common methods<sup>4, 5</sup> described for the study of polymer miscibility are based on the Florry-Huggins theory. According to this theory, the equilibrium melting temperature of a crystalline polymer may be depressed by monomeric diluents incorporated in the polymer. The statistical thermodynamic treatment incorporated in the method takes into account the nature of the polymer and the concentration of the diluent, and also the degree of polymer-diluent interaction. Equation 3.1 describes the Florry-Huggins interaction parameter:

$$\chi = \frac{V_1}{RT} (\delta_1 - \delta_2)^2, \qquad (3.1)$$

where  $V_1$  is the molar volume of the plasticizer; R is the universal gas constant, and  $\delta_1$  and  $\delta_2$  are solubility parameters of the plasticizer and of the polymer, respectively. The smaller the  $\chi$ , the stronger the polymer-diluent interaction and consequently the better the solvent/plasticizer. For example, the  $\chi = 0.55$ designates the dividing line between poor solvents and nonsolvents. Poor solvency usually means 0.31 to 0.55, while  $\chi$  smaller than 0.30 implies a good solvent.

Two methods for determining the interaction parameter were considered: a method based on DSC measurements to determine the depression of the melting temperature of the plasticized samples, and a second method<sup>4</sup> which enables the measurement of this temperature by using optical microscopy. The method based on DSC measurements was selected and used for the determination of Florry-Huggins interaction parameter for PHB/IL1, PHB/ILS, and PHB/TEC

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systems. This method was described for mixtures of PHB with oligo[(R,S)-3hydroxybutyrate]-diol<sup>3</sup>, and is commonly known as Hoffmann-Weeks analysis.

According to this method,  $\chi$  is derived using Equation 3.2:

$$\frac{1}{T_m^{o'}} - \frac{1}{T_m^o} = -\frac{RV_2}{\Delta H_f^o V_1} \times \left[ \left( \ln \frac{\varphi_2}{m_2} \right) + \left( \frac{1}{m_2} - \frac{1}{m_1} \right) \varphi_1 + \chi_{12} \varphi_1^2 \right], \quad (3.2)$$

where  $T_m^{o'}$  and  $T_m^o$  are the equilibrium melting points of the blend and of the crystalline polymer,  $\Delta H_f^o$  is the heat of fusion for the 100 % crystalline polymer,  $V_1$  and  $V_2$  are the molar volumes of repeating units and *m* and  $\varphi$  represent the degrees of polymerization and the volume fractions for each component.

### Experimental details

### **Materials**

PHB (number average molecular weight of 900,000 g/mol) was obtained from Metabolix, Cambridge, MA. The melting point of this PHB sample was 170°C. The polymer was used without further purification and dried at 80°C for three hours in a vacuum oven to ensure the removal of trapped moisture.

1-ethyl-3-methylimidazolium hexafluorophosphate (Figure 3.1a) and 1-butyl-3-methylimidazolium hexafluorophosphate (Figure 3.1b) were purchased from Sigma Aldrich (product numbers 46093, and 70956, respectively). IL1 is solid at room temperature and melts at approximately 58 °C. IL2 is a viscous liquid at room temperature.



Figure 3.1 Structures of a) IL1, and b) II2

Tryethyl citrate (TEC) was obtained from Morflex, Inc., Greensboro, NC (product name Citroflex 2).

# Sample preparation

Samples of pure PHB and PHB containing up to 20 % (weight) ionic liquids or triethyl citrate were prepared by extrusion and injection molding. The PHB powder, previously dried in a vacuum oven at 80 °C for three hours to remove the moisture, was mixed with the ionic liquids by hand and extruded using a DSM micro-extruder (15 cm<sup>3</sup> capacity) (DSM Research B.V., The Netherlands). The temperatures in the three heating zones of the micro-extruder were 195 °C, 185 °C, and 175 °C respectively. The mixtures were extruded at 100 rpm, and the cycle time was three minutes. The extruded polymer systems were injection molded at a fixed temperature of 50 °C.

## **Methods**

a) Mechanical properties evaluation

The flexural strength and modulus of elasticity of the neat and plasticized PHB samples were determined using a United Test System machine, according to ASTM Standard D790. The following testing conditions were chosen for all determinations: load cell of 100 lb, gage length 2 in, test speed: 0.05 in/min.

The notched Izod Impact Strength was measured using an apparatus from Testing Machines Inc., according to ASTM Standard D256, using a load of 1 ft lb. The sample size was  $2.5 \times 0.5 \times 0.125$  (in). Each result represents the average obtained after testing five specimens.

b) Thermal analysis: differential scanning calorimetry and thermomechanical analysis (TMA)

The melting and crystallization behavior of PHB, PHB/IL and PHB/TEC samples were investigated using a 2920 Modulated DSC (TA Instruments). The runs were performed under nitrogen flow, after calibrating the DSC instrument using an Indium standard. For each run, a fresh sample (5-10 mg) cut from injection molded bars was heated from room temperature to 200 °C, kept isothermal for five minutes, in order to remove the thermal history, then cooled to -60 °C, reheated to 200 °C, and cooled to room temperature. The heating and cooling rates were 10 °C/minute.

DSC was also employed for undergoing Hoffman-Weeks analysis. Polymer samples (5-10 mg) were heated from room temperature to 190 °C, kept

isothermal for five minutes, then cooled to different crystallization temperatures  $(T_c)$ , and allowed to crystallize isothermally. The crystallized samples were further re-melted and the new melting points  $(T_m)$  corresponding to each  $T_c$  were recorded.

The glass transition temperatures were also evaluated using a 2940 TMA (TA Instruments). Samples for TMA were cut from injection molded bars using a diamond saw.

### **Results and discussion**

# Modification of properties of PHB by addition of plasticizers

Addition of IL1, IL2, and TEC respectively to PHB leads to decreasing of the flexural strength and modulus, as shown in Figures 3.2 and 3.3. The same decreasing trends were observed for samples containing ionic liquids as for samples containing TEC. At the same time, the notched Izod impact strength of PHB samples did not change significantly after addition of up to 20 % TEC (Figure 3.4), while addition of similar amounts of IL1 and IL2 lead to diminished impact resistance.

The glass transition temperature of PHB/IL1 and PHB/IL2 systems follows the same decreasing trend with increasing amount of potential plasticizer observed for PHB/TEC systems, as shown in Figure 3.5.



**Figure 3.2** Flexural strength of PHB samples containing plasticizing agents



Figure 3.3 Flexural modulus of PHB samples containing plasticizing agents



Figure 3.4 Notched Izod impact strength of PHB samples containing plasticizing agents



Figure 3.5 Glass transition temperatures of PHB samples containing various plasticizing agents Several causes were suspected to determine the decrease of impact strength: solidification of IL1 when cooling the polymer melt: degradation of ILs during the processing of the polymer, inadequate processing conditions, reactions of the ILs with the polymer, lack of miscibility of the polymer with ILs, and changes in the morphology of the polymer. Further investigation determined that the lack of miscibility of the ILs with PHB could be the most significant issue. Hence, a miscibility analysis was performed, through the evaluation of corresponding Florry-Huggins interaction parameters.

Application of Florry-Huggins theory to analysis of miscibility of PHB with two imidazolium phosphates

DSC measurements were performed using TA Instruments equipment, and the equilibrium melting temperature was determined for each of the following systems: PHB/IL1, PHB/10 % IL2, PHB/20 % IL1, PHB/ 5% IL2, PHB/ 13.8 % IL2, and PHB/20 % IL2, according to Hoffmann-Weeks method described above. For comparison, the analysis was done for the PHB/TEC systems (10 % and 20 % TEC in PHB respectively).

The equilibrium melting temperatures of the PHB/plasticizer systems were obtained as the intersections of the  $T_m$  vs  $T_c$  lines with the corresponding  $T_m = T_c$  line (Figure 3.6, and Figure 3.7). The obtained equilibrium melting temperatures are presented in Table 3.2.

**Table 3.2**Equilibrium melting temperatures of PHB samples containing<br/>various plasticizing agents

Polymer System	<i>Т<sub>т,еq</sub></i> [оС]
РНВ	182.93
PHB + 10% IL1	167.91
PHB + 20% IL1	170.49
PHB + 5% IL2	162.19
PHB + 13.8% IL2	162.97
PHB + 20% IL2	162.70
PHB + 10% TEC	180.67
PHB + 20% TEC	178.39



**Figure 3.6** DSC data collected for the determination of equilibrium melting temperatures of PHB containing various potential plasticizers

Based on these temperatures, the calculated Florry-Huggins interaction parameters were: 5.54 for PHB+10% TEC, 2.92 for PHB+20% TEC, and much higher for the polymer systems containing ILs: 35.11 for PHB+5% IL2, 31.68 for PHB+13.8% IL2, and 15 for PHB+20% IL2 . These results indicate a low miscibility of PHB with IL1 and IL2, which is in agreement with the decreasing impact strength measured for the corresponding PHB/IL injection molded samples (Figure 3.4).



Figure 3.7 Extrapolated DSC data for PHB containing IL1, IL2, and TEC

### Conclusions

The ionic liquids investigated in this work as potential plasticizers for PHB, 1-ethyl-3-methylimidazolium hexafluorophosphate and 1-butyl-3methylimidazolium hexafluorophosphate, were found to lack good miscibility with the polymer matrix and to lead to decreased impact properties as compared to pure PHB, and to PHB containing TEC.

### PHB/1-butyl-4-methylimidazolium acetate/xGnP nanocomposites

The results regarding imizadolium hexafluorophosphates and PHB indicated that the compounds screened for a plasticizing effect did not satisfactorily compare to a traditional plasticizer. The search turned to an important characteristic required for a good plasticizer for PHB, which is the ability to form hydrogen bonds with the polymer.

Typically, the anion component of the IL controls the reactivity with water, the coordinating ability, and the hydrophobicity. Common anions that yield useful ILs include hexafluorophosphate [PF6]<sup>-</sup>, tetrafluoroborate, [BF4]<sup>-</sup>, bis(trifyl)imide, [NTf2]<sup>-</sup>, and chloride, Cl<sup>-</sup>. High symmetry pseudo-spherical, non-coordinating anions are commonly regarded as optimal for formation of ILs, the existence of low melting ILs containing anions such as methylsulfate<sup>6</sup>, dicyanamide<sup>7</sup>, and bis(trifluoromethylsulfonyl)imide ([NTf2]<sup>-</sup>)<sup>6, 8</sup>, show that shape and ion-interaction factors are far from clear-cut. The [PF6]<sup>-</sup> and ([NTf2]<sup>-</sup>) anions produce

hydrophobic solvents due to their lack of hydrogen-bond accepting ability<sup>9</sup>, though not all ILs containing these anions are hydrophobic.

The cations can hydrogen bond to the anion. The following scheme was proposed by Wasserchield<sup>6</sup> for ILs containing buthyl-methylimidazolium ([bmim]<sup>+</sup>) cations, as described in Equations 3.3 - 3.6:

$$bmim]^{+} + \cdots A^{-} \Leftrightarrow [bmim]...A$$
 (3.3)

$$K'_{eqm} = \frac{[[bmim]..[A]]}{[bmim^+][A^-]}$$
(3.4)

The cations can also hydrogen bond to the polymer:

$$[\text{bmim}]^+ ] + \text{PHB} \Leftrightarrow [\text{bmim}]...\text{PHB}$$
 (3.5)

$$K'_{eqm} = \frac{\left[ [bmim] ..[PHB] \right]}{\left[ bmim^{+} \right] \left[ PHB \right]}$$
(3.6)

This IL-polymer interaction was described for methyl methacrylate, and it occurs via hydrogen bond formation between the cation and the carbonyl oxygen of the electron withdrawing group. This clearly indicates that there is a competition between the anion and the solute for the proton.

The focus remained on imidazolium-containing ionic liquids since they are better characterized, and more readily available with a large range of anions. 1-butyl-4-methylimidazolium acetate (IL3) was chosen as a potential plasticizer for PHB because the anion does not contain halogens, and is considered non-toxic. The adsorption of IL3 onto xGnP-1 surfaced, and effects of IL3 on PHB were investigated and are reported here.

# **Experimental details**

# **Materials**

PHB (number average molecular weight 900,000 g/mol, melting point 170 °C) was obtained from Metabolix, Cambridge, MA. The polymer was used without further purification and dried at 80 °C for three hours in a vacuum oven to ensure the removal of trapped moisture. The exfoliated graphite nanoplatelets having an average size of 1  $\mu$ m (xGnP-1) was produced in-house<sup>10,11</sup> starting from GraphGuard<sup>TM</sup> 160-50A acid intercalated graphite produced by Graftech (Cleveland, OH).

1-butyl-4-methylimidazolium acetate was purchased from Sigma Aldrich (product number 39952).

# Sample preparation

a) Surface treatment of xGnP-1 with IL3

1 g of dried xGnP-1 was immersed in 5 ml IL3, sonicated for 10 minutes, and allowed to age for 24 hours at room temperature. The excess IL3 was removed by washing with acetone/water, and the xGnP-1 particles were filtered and dried in a vacuum oven for three hours in order to evaporate the remaining solvent.

b) Injection molded PHB/IL3 samples

Samples of pure PHB and PHB containing 1 % wt IL3 were prepared by extrusion and injection molding. The PHB powder, previously dried in a vacuum oven at 80 °C for three hours to remove the moisture, was mixed with IL3 and extruded using a DSM micro-extruder (15 cm<sup>3</sup> capacity) (DSM Research B.V., The Nederlands). For the extrusion of pure PHB, the temperatures in the three heating zones of the micro-extruder were 175 °C, 185 °C, and 195 °C respectively. The mixtures were extruded at 100 rpm, and the cycle time was three minutes. The temperature of the mold was 50 °C. Various extrusion conditions were attempted for PHB/IL3 samples, as described in the *Results and discussion* section below.

### <u>Methods</u>

a) Thermal analysis: Differential Scanning Calorimetry

The melting and crystallization of PHB, and PHB/IL3 samples were analyzed using differential scanning calorimetry, using the same equipment and procedure as described in the preceding section.

### b) Molecular weight determination using dilute solution viscometry

Dilute solution viscometry is a technique commonly used to determine the molecular weight of polymers by calculating the intrinsic viscosity of a dilute solution of polymer in an adequate solvent, based on the efflux time. The specific viscosity of the polymer solution in chloroform was determined based on the efflux time (Equation 3.7):

$$\eta_{sp} = \frac{t - t_0}{t_0} \,, \tag{3.7}$$

where *t* is the efflux time of polymer solution, and  $t_0$  is the efflux time of pure solvent. The reduced viscosities were calculated using Equation 3.8.

$$\eta_{red} = \frac{\eta_{sp}}{C}, \qquad (3.8)$$

where C is the concentration of polymer in solution, and  $\eta_{red}$  is given in in dl/g.

The intrinsic viscosity,  $[\eta]$  is determined from the intercept of the line obtained by plotting the reduced viscosity versus concentration, and by applying the Mark-Houwnik-Sakurada (M-H-S) equation (Equation 3.9) the molecular weight can be estimated.

$$[\eta] = \mathbf{K} \cdot \mathbf{M}_{\mathbf{w}}^{\alpha}, \tag{3.9}$$

The M-H-S parameters for PHB<sup>12</sup> are as follows:  $K = 7.7 \cdot 10^{-5}$ ;  $\alpha = 0.82$ , and  $[\eta] = 7.7 \cdot 10^{-5} \cdot M_w^{0.82}$ .

The maximum concentrations ( $C_{max}$ ) of PHB solution in chloroform and PHB+1%IL3 in chloroform were 1.00 g/dl respectively. The solvent efflux time was 133 seconds for each case.

DSV measurements were performed using Ubelohde tubes types Cannon 0C an Cannon 0. The temperature was maintained at 77 °F using a heater and a water bath. To ensure the reproducibility and accuracy of the results, the solvent efflux time was measured three times for each concentration, and averaged for each set of measurements.

For a solution volume of 14 ml, the following dilution scheme was applied:

- introduce 14.0 mL solution (C<sub>max</sub>);
- remove 4.0 mL and replace with 4.0 mL solvent (5Cmax/7 =  $0.714 C_{max}$ );
- remove 4.0 mL and replace with 4.0 mL solvent (25Cmax/49 = 0.510 Cmax);
- remove 4.0 mL and replace with 40 mL solvent (125Cmax/343 = 0.364 Cmax);
- remove 4.0mL and replace with 4.0 mL solvent (625Cmax/2401 = 0.260 Cmax);
- remove 8.0 mL and replace with 8.0 solvent (0.4 \* last value = 0.104 Cmax).

## c) X-Ray Photoelectron Spectroscopy

X-Ray Photoelectron Spectroscopy (XPS) was used for the evaluation of xGnP-1, and xGnP-1 surface treated IL3. A Physical Electronics Phi 5400 ESCA system with a non-monochromatic magnesium K $\alpha$  X-ray source was used for analyzing samples at pressures between 10<sup>-9</sup> and 10<sup>-8</sup> Torr, with a pass energy of 29.35 eV, and a take-off angle of 45°. Atomic concentrations were determined using previously determined sensitivity factors. All peaks were referenced to the signature C1s peak for adventitious carbon at 284.6 eV.

d) Evaluation of mechanical properties

The flexural strength, modulus, and the notched Izod impact strength of PHB, PHB containing 3 % wt xGnP-1, and 3 % wt xGnP-1 surface treated with IL3 were measured as described in the first section of the present chapter.

# Results and discussion

Processing of PHB in the presence of amounts of IL3 as low as 1 wt % was not possible under the extrusion condition previously optimized for PHB alone. The viscosity of the PHB/IL3 melt dropped dramatically upon heating in the mini-extruder. The first indicator for decreasing viscosity was the drop in the force measured in the extruder (Table 3.3)

Sample	Temperature [°C]			Force	Remarks
	Zone 1	Zone 2	Zone 3	[N]	i tomano
PHB	195	185	175	1200	Optimized conditions
PHB+1% IL3	195	185	175	225	
PHB+1% IL3	185	175	165	220	Not able to
PHB+1% IL3	175	175	175	200	extrude/injection mold.
PHB+1% IL3	175	165	165	200	Very low viscosity
PHB+1% IL3	175	165	165	200	

Table 3.3	Processing conditions and forces recorded by the DSM extruder for
	PHB, and PHB containing IL3

The low PHB viscosity in the presence of IL3 indicated possible degradation of PHB. Typical DSC runs (Figure 3.8) indicated that the melting point of PHB dramatically decreased in the presence of 1 wt % IL3, from 173 °C to 146 °C, while the crystallization of PHB from the melt was also affected.



Figure 3.8 DSC traces for PHB and PHB containing IL3

The dilution schemes for PHB and PHB containing 1 wt % IL3 in chloroform are shown in Tables 3.4 and 3.5.

 Table 3.4
 Dilution scheme and dilute solution viscometry results for PHB in chloroform

Concentration [g/dl]		Time t [s]	$\eta_{sp}$	$\eta_{ m red}$
C <sub>max</sub>	1.0500	404.33	2.0401	1.9430
0.714 C <sub>max</sub>	0.7497	349.67	1.6291	2.1730
0.510 C <sub>max</sub>	0.5355	300	1.2556	2.3448
0.364 C <sub>max</sub>	0.3822	270	1.0301	2.6951
0.260 C <sub>max</sub>	0.2730	245	0.8421	3.0846
0.104 C <sub>max</sub>	0.1092	191.33	0.4386	4.0165

Table 3.5Dilution scheme and dilute solution viscometry results for PHB<br/>containing 1 wt % IL3 in chloroform

Concentration [g/dl]		Time t [s]	$\eta_{sp}$	$\eta_{ m red}$
C <sub>max</sub>	0.1500	135.67	0.0463	C <sub>max</sub>
0.714 C <sub>max</sub>	0.1071	134	0.0334	0.714 C <sub>max</sub>
0.510 C <sub>max</sub>	0.0765	132.67	0.0231	0.510 C <sub>max</sub>
0.364 C <sub>max</sub>	0.0546	132	0.018	0.364 C <sub>max</sub>
0.260 C <sub>max</sub>	0.0390	132.33	0.0129	0.260 C <sub>max</sub>

The intrinsic viscosity of PHB, calculated based on the measurements presented in Figure 3.9, was  $[\eta] = 3.7405$ , and corresponded to a weight average molecular weight of 519,000 g/mol.



Figure 3.9 Determination of the intrinsic viscosity of processed PHB

The intrinsic viscosity of PHB containing 1 % IL3, calculated based on the measurements presented in Figure 3.10, was  $[\eta] = 0.2413$ , and corresponded to a weight average molecular weight of 18,340 g/mol. Hence, the molecular weight of PHB decreased from approximately 519,000 g/mol to approximately 18,340 g/mol after the addition of 1 % (wt) of IL3.



Figure 3.10 Determination of the intrinsic viscosity of processed PHB containing 1 wt % IL3

### Surface treatment of xGnP-1 with IL3

The surface treatment of xGnP-1 with IL3 was designed so that one could introduce in the PHB/xGnP system a small amount of ionic liquid and one could control the localization of the IL at the PHB/xGnP-1 interface. It was hoped that the degradation of PHB in the presence of IL would affect the polymer chains in the very proximity of the xGnP-1, and the resulted lower molecular weight polymer at the interface with the carbon nanoplatelets will lead to better properties of the nanocomposites.

The results of the XPS evaluation of the surface treatment are presented in Table 3.6, which shows the atomic concentrations of xGnP-1 surfaces, as well as of xGnP-1 surface treated with IL3. These results indicate that after the surface treatment, the amount of nitrogen on the surface of xGnP-1 increases. This is

attributable to the nitrogen atoms in the imidazolium ring. The presence of zirconium, only detected on the untreated xGnP-1, is due to the final stage of xGnP-1 preparation, during which the size of xGnP is reduced from ~15  $\mu$ m to ~1  $\mu$ m in a vibratory mill that uses zirconium oxide milling balls was employed. No Zirconium was detected on the surface treated xGnP-1, which indicates that this residue was completely removed during the washing steps incorporated in the surface treatment process.

Table 3.6	Atomic concentration for exfoliated graphite nanoplatelets surfa-	ce
	treated with IL3 (XPS results)	

Sample	C1s	N1s	01s	Other
xGnP-1	92.62	0.45	6.71	Zr3d 0.22
XGnP/IL3	91.89	0.84	7.27	-

### Mechanical properties of PHB/xGnP-1/IL3 nanocomposites

The flexural strength, the modulus and the notched izod impact strength of PHB, PHB containing 3 % wt xGnP-1 and PHB containing 3 % et xGnP-1 surface treated with IL3 were measured. The results, presented in Figure 3.11, 3.12, and 3.13, indicate that the adsorption of IL3 onto the surface of xGnP did not lead to improved mechanical properties of the corresponding PHB/xGnP-1 nanocomposites.



Figure 3.11 Effect of surface treatment of xGnP-1 with IL3 on the flexural strength of PHB/xGnP-1 nanocomposites



Figure 3.12 Effect of surface treatment of xGnP-1 with IL3 on the modulus of PHB/xGnP-1 nanocomposites



Figure 3.13 Effects of surface treatment of xGnP-1 with IL3 on the notched Izod impact strength of PHB/xGnP-1 nanocomposites

## Conclusions

Processing of PHB nanocomposites using ionic liquids was not reported before this study. A review of the literature identified ionic liquids as potential additives for PHB/xGnP nanocomposites that through plasticization can modify the properties of the biopolymer, and through surface modification can be used to change the surface of the exfoliated graphite nanoplatelets and hence the polymer/xGnP interaction. The three ionic liquids investigated did not lead to beneficial results on the properties of PHB/xGnP nanocomposites. The two imidazolium phosphates were shown to be insufficiently miscible with the PHB, which in turn lead to reduced impact properties. The imidazolium acetate, also explored as a surface treatment agent for the xGnP, was proven to degrade PHB, and to detrimentally affect the mechanical properties of the corresponding PHB/xGnP nanocomposites. A fundamental understanding of the relation between the structure of ionic liquids and their effect on the polymer, together with the study of all the factors governing the system behavior, may eventually allow the determination of ionic liquids which could, at the same time, act as plasticizers for thermoplastic PHB matrix, and as surface modification agent for the xGnP.

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### **CHAPTER 4**

# POLYLACTIC ACID/ EXFOLIATED GRAPHITE NANOPLATELET NANOCOMPOSITES

# Introduction

The nucleating effect of exfoliated graphite nanoplatelets on PHB, described in Chapters 2 and 3, motivated the investigation of the consequences of the heterogeneous nucleation on the properties of resultant nanocomposites. This study refers to composites obtained from another semicrystalline polymer derived from renewable resources, PLA, and xGnP. The investigations focus on the relations between processing methods, dispersion of xGnP, and properties of the nanocomposites. The results underline the importance of optimized mixing of xGnP with PLA, and the immediate consequences of dispersion of xGnP on the mechanical properties of the composites, and provide the basis for the investigation of the nanoscale structure of PLA/xGnP nanocomposites (Chapter 6).

Previous results obtained in the Drzal group for PP/xGnP<sup>1-3</sup> composites indicate a strong dependence of the properties on the processing methods and crystallization conditions.<sup>4, 5</sup>

We report here on the properties of PLA/xGnP composites prepared using three different processing methods: extrusion and injection molding, pre-mixing and compression molding, and solvent mixing and compression molding.

# **Experimental details**

# **Materials**

Injection molding-grade polylactide, PLA 3001D, was obtained from NatureWorkIs<sup>®</sup>LLC (Minneapolis, MN), and used without further purification. Exfoliated graphite nanoplatelets having an average size of 1 μm (xGnP-1) were produced in-house as described in Chapter 2. PLLA was purchased from Boehinger-Ingleheim Chemicals (Petersburg, VA). Two different molecular weight PLLA samples were used in this study: RESOMER<sup>®</sup> L209S (intrinsic viscosity 3.0 dl/g for 0.1 % solution in chloroform at 25 °C), and RESOMER<sup>®</sup> L210S (intrinsic viscosity 3.8 dl/g for 0.1 % solution in chloroform at 25 °C). Methylene chloride and 2-propanol were purchased from Sigma Aldrich.

### Sample preparation

### a) Extrusion and injection molding

Samples of pure PLA 3100D and PLA 3100D containing, 1 % wt – 10 % wt xGnP-1 were prepared by extrusion and injection molding. The PLA pellets, previously dried in a vacuum oven at 80  $^{\circ}$ C for three hours to remove moisture,

were mixed with the xGnP-1 and extruded using a DSM micro-extruder (15 cm<sup>3</sup> capacity) (DSM Research B.V., The Nederlands). The temperature in each of the three heating zones of the micro-extruder was 200 °C. The mixtures were extruded at 150 rpm, and the cycle time was three minutes. A transfer cylinder heated at 193 °C was used to transfer the extruded polymer systems into the injection molding machine. The optimized injection molding pressure and the mold temperature were 80 psi, and 25 °C, respectively.

# b) Pre-mixing and compression molding

In an attempt to improve the dispersion of xGnP-1 in polylactides, samples of neat PLA L210S and PLA L210S/xGnP-1 nanocomposites containing 1 % wt to 8 % wt xGnP-1 were prepared by pre-mixing the polymer and the xGnP-1 in isopropanol, a non-solvent for PLA, but a good dispersion medium for xGnP-1, as follows. For preparing 1 g PLA L210S/xGnP-1 nanocomposite mixture, appropriate amounts of xGnP-1 were dispersed in 100 ml isopropanol by sonication. A VirSonic 100 Cell Disrupter from Virtis (Gardiner, NY) equipped with a 0.5 inch probe was used for 10 minutes. Corresponding amounts of PLA L210S/isopropanol dispersions were then mixed together and sonicated for an additional 10 minutes. The isopropanol was removed by overnight evaporation in the hood, then the PLA/xGnP-1 mixtures were dried in a vacuum oven (20 hours at 80 °C) prior to compression molding.

The dried PLA/xGnP-1 mixtures were compression molded at 200 °C for 2 min, under an applied pressure of 18,000 psi, using a Carver laboratory press (Carver Inc., Wabash, IN). The platens of the press were pre-heated to 200 °C prior to compression molding.

### c) Solution mixing and compression molding

PLA L209S, PLA L210S, and their composites containing with xGnP-1 were also prepared by solution mixing and compression molding. The xGnP-1 loading varied from 0 wt % to 9 wt % for both PLA samples (L209S and 210S). For each xGnP-1 loading, 1 g of PLA/xGnP-1 mixture was prepared as follows: appropriate amounts of xGnP-1 were dispersed in 20 mL methylene chloride by sonication (5 min, 10 W) using a VirSonic 100 Cell Disrupter from Virtis (Gardiner, NY). Corresponding amounts of PLA were further dissolved in the xGnP-1/ methylene chloride dispersions, and the obtained PLA/xGnP-1 mixtures were precipitated using 2-propanol. The resulted PLA/xGnP-1 materials were kept at room temperature overnight, and then dried in a vacuum oven at 80 °C for 20 h to ensure the complete evaporation of the organic solvents. The dried PLA/xGnP-1 mixtures were compression molded at 200 °C for 2 min, under an applied pressure of 18,000 psi, using a Carver laboratory press (Carver Inc., Wabash, IN). The platens of the press were pre-heated to 200 °C prior to compression molding.

### <u>Methods</u>

### a) Flexural strength and modulus evaluation

The flexural strength and modulus of the neat PLA 3100D and PLA 3100D/xGnP-1 injection molded samples were determined using a United Test System machine, according to ASTM Standard D790. The following testing conditions were chosen for all determinations: load cell of 100 lb, gage length 2 in, test speed: 0.05 in/min.

### b) Dynamic mechanical analysis

The storage moduli of PLA L209S, PLA L210S, and the corresponding and composites with xGnP-1 were evaluated using a 2980 Dynamic Mechanical Analyzer (TA Instruments, New Castle, DE). The samples (approximately 5.50 mm x 16 mm x 0.10 mm) were cut from the compression molded films, and tested in tension during heating from room temperature to 120 °C. The reported values are for storage modulus at room temperature, and represent the average of three measurements per xGnP-1 concentration in the PLA.

### c) Nanoindentation

The microscale determination of Young's modulus and hardness of PLA L210S and PLA L210S/xGnP-1 composites were conducted using a MTS-Nanoindentation System (MTS Nano Instruments, Oak Ridge, TN) equipped with a Berkovich type diamond tip. An XP module, allowing a maximum indentation

depth of 5000 nm, was employed. The samples investigated were PLA/ composite films of 0.13±0.1 mm thickness. 25 indents were, 25 mm apart were set for each sample, with a testing depth of 2000 nm.

### d) Differential scanning calorimetry

The melting and crystallization of PLA 3100D, PLA L209S, PLA L210S, and their composites with xGnP-1 were analyzed using a 2920 Modulated DSC (TA Instruments, New Castle, DE). The runs were performed under nitrogen flow, after calibrating the DSC instrument using an Indium standard. For each run, a fresh sample (6-10 mg) of polymer/ composite was placed in a seal aluminum pan and subjected to two heating/ cooling cycles. During the first cycle, incorporated in the DSC method to ensure the erasure of samples' thermal history, the samples were heated (10 °C/min) from room temperature to 200 °C, kept isothermal at 200 °C for 10 min, cooled (10 °C/min) to 0 °C, and equilibrated at 0 °C. The second heating/cooling cycle immediately followed and involved heating (3 °C/min) to 200 °C, keeping the samples isothermal at 200 °C, then cooling (3 °C) to room temperature. Unless specified otherwise, the data reported and analyzed refer to the second heating/ cooling cycle.

# e) Electrical conductivity evaluation

Impedance Spectroscopy – two-point method – was employed to determine the resistivity of PLA/xGnP-1 injection molded composites along the flow direction. Samples (approximately 3x5x12 mm) were cut from the center parts of

injection molded bars using a diamond saw. In order to ensure good contact between the polymer/composite samples and the electrodes, the composite surfaces in contact with the electrodes were first subjected to oxygen plasma treatment (ten minutes at 550 W), then coated with gold (1-2 nm coating thickness). The electrical resistance was measured in the frequency range from 0.1 to 100,000 Hz. The reported results are average values for measurements on five distinct samples for each xGnP-1 concentration in PLA, and represent bulk electrical conductivity (converted from resistance by taking into account the samples' dimensions).

### f) Optical microscopy

The samples for optical microscopy were prepared as thin polymer films by heating very thin sections of PLA/xGnP-1 injection molded bars in a Mettler Toledo FP82 hot stage. Specifically, the polymer was placed on glass slide, covered with glass cover slip, and heated at a rate of 20 °C/minute from room temperature to 190 °C, kept isothermal for three minutes, then either allowed to crystallize upon cooling to room temperature, or to crystallize isothermally at different preset crystallization temperatures. The morphology of PLA and the size of the spherulites were observed using an Olympus BH2 optical microscope equipped with a Spot<sup>™</sup> camera.

### **Results and discussion**

#### Properties of injection molded PLA 30001D/xGnP-1 nanocomposites

Hot stage optical microscopy observations of PLA and PLA/xGnP-1 systems crystallized from the melt under both isothermal and nonisothermal conditions revealed that the injection molded grade PLA was nucleated by xGnP-1. Figure 4.1 shows optical micrographs of PLA 3001 D and its composites with xGnP-1 isothermally crystallized from the melt. The neat polymer did not show any crystalline structures after being cooled from 200 °C and kept at 140 ° for 10 minutes. Under the same isothermal crystallization conditions, large spherulites were observed in the presence of small amounts (0.01 % wt) of xGnP-1 (Figure 4.1a). As the amount of xGnP-1 in the PLA increased, spherulitic structures were no longer observable (Figure 4.1c,d).



Figure 4.1 Optical micrographs showing PLA/xGnP-1 composites crystallized from the melt under isothermal conditions. The amount (wt %) of xGnP-1 was a) 0 %; b) 0.01 % c) 1 % and d) 10% The crystallinity of extruded and injection molded PLA/xGnP-1 composites containing 1 % wt xGnP-1 was 144 % higher than that of the neat PLA but increasing amounts of xGnP-1 did not increase the crystallinity (Figure 4.2). These results are similar to the results obtained for PHB/xGnP-1 systems (Chapter 2).



**Figure 4.2** Degree of crystallinity of PLA/xGnP-1 composites prepared by extrusion and injection molding

For PLA 3001D/xGnP-1 nanocomposites prepared by extrusion and injection molding, an improvement in flexural modulus was only detected when the concentration of xGnP-1 in PLA 3001D exceeded 4 wt % (Figure 4.3). The maximum improvement in modulus was approximately 70 % for 8 - 9 % wt xGnP-1 (~ 11 - 13 % vol). For comparison, 10 % vol xGnP-1 in a PP matrix lead

to approximately 200 % improvement in flexural modulus of the injection molded PP/xGnP-1 nanocomposites.<sup>6</sup> The two systems are however difficult to analyze side-by-side for several reasons. Both matrices are commercial-grade, and might contain additives affecting their crystallization behavior. The polylactide contains a mixture of *D*- and *L*- stereoisomers in an unknown ratio. The poly(*D*-lactic acid) (PDLA) component increases the amorphous contents and limits the ability of the matrix to crystallize. The PP, as a result of the polymerization reaction, is likely to contain catalyst particles, which increase the nucleation density of the neat polymer. If xGnP agglomerates at higher loadings and polymer-rich regions are created in the composites, it is more likely for the PP than for the PLA chains that are not in the vicinity of xGnP to nucleate and crystallize. Nevertheless, the xGnP was shown to nucleate the  $\beta$ -form of PP crystals<sup>4</sup>, which determines better mechanical properties than those of the more common  $\alpha$ - form, and account for further improvement in modulus.

Differences in dispersion of the xGnP-1 in PLA and PP might be due to the melt flow index of the two polymers. The melt flow index at the processing temperature is higher (up to 30 g/10 minutes) for the PLA used than for the PP (12 g/10 minutes).

Micromechanical models used to predict the properties of polymer composites<sup>7</sup> severely overestimated both the value of PP/xGnP-1<sup>6</sup> and PLA 3001D/xGnP-1 composites.

The flexural strength of the PLA 3001D/xGnP-1 composites did not differ significantly from that of neat PLA 3001D (Figure 4.3).



Figure 4.3 Flexural moduli of PLA 3001D and PLA 3001D /xGnP-1 nanocomposites prepared by extrusion and injection molding



Figure 4.4 Flexural strength of PLA 3001D and PLA 3001D /xGnP-1 nanocomposites prepared by extrusion and injection molding
The percolation threshold for electrical conductivity in injection molded PLA/xGnP-1 nanocomposites was approximately 9 % wt (~ 12 % vol) (Figure 4.5). The electrical conductivity of PLA/xGnP-1 composites was found to be similar to that of injection molded PP/xGnP-1 composites, which also had a high percolation threshold of 9 % vol.



Figure 4.5 Bulk electrical conductivity of injection molded PLA 3001D /xGnP-1 nanocomposites

The exfoliated graphite nanoplatelets were shown to improve the modulus of neat PLA, as well as to impart electrical conductivity, but at very high loadings. The need of property improvement with smaller addition of nanoplatelets directed the study towards exploring alternative processing methods, with emphasis on dispersion of the nanoplatelets. Properties of PLA L210S/xGnP-1 nanocomposites prepared by pre-mixing and compression molding

The goal of pre-mixing the PLA with the graphite nanoplatelets was to improve the dispersion of the xGnP.

The results of dynamic mechanical analysis of PLA L210S and its composites containing up to 11 % wt xGnP-1 did not indicate any improvement in the modulus of PLA L210S after the addition of xGnP, and even lower moduli for samples containing over 4 % wt xGnP-1 (Figure 4.6). These poor mechanical properties were attributed to agglomeration of the graphite nanoplatelets in the PLA matrix.



**Figure 4.6** Moduli of PLA L210S and PLA L210S/xGnP-1 composites prepared by pre-mixing and compression molding, as determined by DMA

Nanoindentation experiments further confirmed the poor dispersion. Figure 4.7 shows the moduli of PLA L210S and its composites with xGnP-1, as determined from nanoindentation. These results indicate a slight improvement of modulus of the surfaces of PLA L210S composites containing 4 % wt xGnP-1, followed by a drop of moduli values for amounts of nanoplatelets exceeding 4 % wt – a trend similar to the one observed for the DMA results. The decrease in surface mechanical properties for higher amounts of xGnP-1 was observed for the surface hardness measured concomitantly in the nanoindentation experiments (Figure 4.8).



Figure 4.7 Moduli of PLA L210S and PLA L210S/xGnP-1 composites, as determined from nanoindentation experiments



Figure 4.8 Surface hardness of PLA L210S and PLA L210S/xGnP-1 composites, as determined from nanoindentation experiments

Both DMA and nanoindentation results for PLA L210S/xGnP-1 nanocomposites prepared by pre-mixing and compression molding indicate poor dispersion of xGnP in the polylactides. A DSC analysis of the nonisothermal crystallization from the melt for PLA L210S and composites containing xGnP-1 (Figure 4.9) showed that the neat PLA L210S crystallizes from the melt at around 110 °C. Addition of 1 % xGnP-1 leads to a bimodal crystallization peak. The same bimodal behavior was observed for higher amounts of xGnP-1 in the polylactide, indicating two competing types of nucleating behavior – a homogeneous nucleation mechanism, reflected by the peak occurring at lower temperatures, and a heterogeneous nucleation mechanism, reflected by the higher temperature nonisothermal crystallization peaks.



Figure 4.9 DSC traces for the nonisothermal crystallization from the melt of PLA L210S, and PLA L210S containing xGnP-1

Figure 4.10 and 4.11 show that the two crystallization peaks are similar in terms of peak area and full-width-at-half-maximum (FWHM) for 1 % wt xGnP-1 in the polylactides. As the amounts of xGnP-1 increase, the higher-temperature peak (corresponding to heterogeneous nucleation by the nanoplatelets), becomes smaller than the accompanying peak (assigned to homogeneous nucleation). This indicates amounts of xGnP-1 higher than 1 % wt lead to both heterogeneous nucleation of the polylactides, and retardation of crystal growth. Similar combination of nucleating effect and retardation of crystal growth was observed in other nanocomposites obtained from semicrystalline polymers, for example intercalated poly(ethylene oxide)/montmorillonite<sup>8</sup>, and PCL/montmorillonite.<sup>9</sup>



Figure 4.10 Areas of peaks corresponding to nonisothermal crystallization from the melt of PLA L210S, and PLA L210S/xGnP-1 composites



Figure 4.11 Full-width-at-half-maximum values of the crystallization peaks corresponding to PLA L210S, and PLA L210S/xGnP-1 composites

The mechanical properties and the crystallization behavior of PLA L210S/xGnP-1 composites prepared by pre-mixing and compression molding indicated poor dispersion of the xGnP-1 in the polylactides, due to agglomeration of the xGnP-1, and retardation of crystal growth. Figure 4.12 summarizes the calculated degree of crystallinity of these composites, as calculated from using the enthalpy of melting obtained from DSC scans. Addition 1 % wt xGnP-1 lead to a 123 % increase in crystallinity as compared to the neat PLA. Amounts of xGnP-1 higher than 1 % wt did not conduce to further increase in the overall degree of crystallinity. The differences in mechanical properties are likely to be related to the quality of the crystal structures formed.



Figure 4.12 Degree of crystallinity of PLA/xGnP-1 composites prepared by premixing and compression molding

# <u>Properties of PLA L210S/xGnP-1 nanocomposites prepared by solution</u> mixing and compression molding

The use of solvents mediums to mix polymers and nanoparticles is a very efficient way to achieve good dispersion of nanoparticles, but very frequently a less green approach, mainly because of the toxicity of commonly used solvents, and difficulty and cost of solvent recovery procedures.

For the preparation of PLA/xGnP composites, solution mixing was the last method considered since the search for a solvent that at the same time dissolves the polylactides and provides a good dispersion medium for the graphite nanoplatelets lead to chlorinated compounds such as chloroform, and methylene chloride, which are very volatile, and toxic.

Dynamic mechanical analysis revealed that the storage moduli of PLA L210S/xGnP-1 composites prepared by solution mixing and compression molding was significantly higher than moduli of corresponding composites prepared by pre-mixing and compression molding, as shown in Figure 4.13.

The analysis of the fracture surfaces of PLA/xGnP-1 composites containing over 1 % wt xGnP-1 did not lead to observations that could be related to the differences in the properties of the composites prepared using the two approaches. Important differences between the pre-mixed and the solution-mixed samples were revealed by differential scanning calorimetry, which is a bulk characterization technique, and were further refined using a localized thermal analysis method that was adapted for the characterization of PNC, as described in Chapter 6.



Figure 4.13 Storage moduli of compression molded PLA L210S and PLA L210S/xGnP-1 composites prepared using two mixing approaches

#### Conclusions

Solution mixing followed by compression molding leads to the best dispersion of xGnP-1 in the PLA. Amounts of xGn\_1 exceeding 3 % wt lead to agglomeration of xGnP and appear to determine two competing processes: nucleation of the polymer matrix, and retardation of crystal growth. The competition between the two processes, and the consequences on the nanoscale structure of the PLA/xGnP-1 composites, are further described in Chapter 6.

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# **CHAPTER 5**

# THERMAL CONDUCTIVITY OF POLYLACTIC ACID/EXFOLIATED GRAPHITE NANOPLATELET NANOCOMPOSITES

## Introduction

Incorporation of micro- and nano-size fillers with high thermal and electrical conductivities in polymer matrices is expected to lead to composite materials with improved thermal and electrical conductivity compared to the neat polymers. This study describes the experimental determination of the thermal conductivity of PLA composites with xGnP-1 and xGnP-15, and presents a new approach suggested for the preparation of composites with high thermal conductivity using morphology direction in biphasic polymer blends.

Carbon-based reinforcements are widely used for applications requiring polymer composites with enhanced thermal and electrical performance. Carbon fibers and carbon black are traditional fillers for polymer composites and were shown to lead to materials with increased thermal conductivity. The thermal conductivity along the graphene plane (Table 5.1 and Table 5.2) makes carbonbased nanosize reinforcements, among which exfoliated graphite nanoplatelets, attractive additives for PNC having high thermal conductivity. The most recently

reported results for room temperature thermal conductivity of a suspended single-layer graphene<sup>1</sup> indicate that a conductivity value in the range from  $(4.84\pm0.44)\times10^3$  to  $(5.30\pm0.48)\times10^3$  W/mK.

Table 5.1	Room temperature thermal conductivity of materia	als of	various
	crystalline structures		

Material	K (Wm <sup>-1</sup> K <sup>-1</sup> )		
Diamond	600		
Graphite (parallel to c-axis)	3550		
Graphite (normal to c-axis)	89		
SiC (single crystal)	~100		
SiC (polycrystal)	~10-50		
Epoxy resins	0.2 – 0.5		
Polyesters	0.2 - 0.24		

Nanosize fillers are largely used for improving thermal and electrical properties of polymers<sup>2</sup>, the advantages of using smaller particles coming mainly from the large surface area. Recently, Winey et al.<sup>3</sup> summarized studies on improvements in thermal conductivity of polymers by incorporating CNT, underlining that while PNC incorporating CNT have low percolation thresholds for electrical conductivity, the thermal conductivity fails to show similar improvement.

 Table 5.2
 Properties of various nanosize fillers used for improving thermal and electrical conductivities of polymers

Filler	Shape (approx.)	Smallest dimension (nm)	Aspect ratio	E (GPa)	Electrical conductivity (S/cm)	Thermal conductivity (W/mK)
Carbon nanofiber	rod	50-100	50-200	500	700-1000	10-20
Carbon MWNT	rod	5-50	100 – 10,000	1,000	500 – 10,000	100 - 1000
Carbon SWNT	rod	0.6 – 1.8	100 – 10,000	1,500	1000 - 10,000	1000
Aluminisillicate nanoclay	plate	1 – 10	50 100	200 – 250		1 -10
Nano-TiO2	sphere	10 -40	~1	230,000	$10^{-11} - 10^{-12}$	12
Nano-Al <sub>2</sub> O <sub>3</sub>	sphere	50-100	~ 1	50	20 - 30	20 - 30

Extensive research was devoted to understanding the reasons why in polymer/CNT composites the thermal conductivity improvement is not as sharp as the corresponding improvement in electrical conductivity. The main reason<sup>4</sup> for the difference between thermal and electrical transport in composites incorporating high aspect ratio CNT is thought to be the relatively small difference between the thermal conductivity of the matrix and the thermal conductivity of the CNT ( $\lambda_{CNT}/\lambda_{polymer} \sim 10^4$ ). The corresponding ratio of electrical conductivities is  $\sim 10^{12} - 10^{16}$ . The heat transfer is more likely to involve the polymer matrix. Secondary reasons are the interfacial thermal resistance for the heat flow between the CNT and the polymer/carbon nanotube interfacial thermal

resistance. Huxtable et al.<sup>5</sup> determined that in polymer/CNT composites the nanotubes-polymer interfacial thermal resistance is 12 MWm<sup>-2</sup>K<sup>-1</sup>, and the interfacial thermal resistance between CNT is also very high.

Heat transfer through materials occurs through transmission of phonons – lattice vibrations –, and free electrons (if present). The phonons and the free electrons are heat carriers. From a kinetic point of view, these carriers have a mean free path  $\lambda$  between collisions (energy exchange events), and an average velocity v. The kinetic theory defines the thermal conductivity, *K* (Equation 3.1).

$$K = \frac{1}{3} c \nu \lambda , \qquad (5.1)$$

where *c* is the volume specific heat of the carrier concerned.<sup>6</sup> The carriers' average velocities are very insensitive to temperature. Since polymers do not have free electrons, in order to understand the mechanism of heat transfer in polymer composites one needs to focus on the phonons as carriers. Phonon velocity (speed of sound) is higher in light, stiff materials. The mean free path of phonons is very structure-sensitive and can be very high in specimens of high perfection and large grain size. Table 5.1 offers some examples in this respect. Crystalline polymers have slightly higher thermal conductivity than amorphous ones. For filled semicrystalline polymers, it is extremely important to understand how the fillers, regardless of their size, affect the crystalline structure, since this governs the transport properties.

PLA and PHB are thermoplastic polyesters and act as insulators for electricity and heat. Their transport properties have a direct relationship to their crystalline

structure, and can be tailored by incorporating fillers specific to desired applications. Exfoliated graphite nanoplatelets have a high thermal conductivity and when combined with semicrystalline PLA matrix, nanocomposites with enhanced thermal conductivity are expected. The present study aims to compare the effect of exfoliated graphite nanoplatelets of two different sizes on the thermal and electrical conductivities of PLA.

The experimental results obtained for the thermal conductivity of PLA/xGnP composites presented here indicated the possibility of a percolating mechanism for the thermal conductivity and the need for strategies that could allow control over morphology and preferable alignment of graphite nanoplatelets along continuous paths.

Several examples are reported in the literature where composites of conductive fillers and nearly immiscible biphasic polymer blends (containing usually a semicrystalline polymer and an amorphous polymer) showed very good control of electrical conductivity and low percolation thresholds. In such biphasic systems, the conductive filler localizes either in the semicrystalline matrix (Figure 5.1a) or at the interface between the amorphous polymer and the semicrystalline polymer (Figure 5.1b).<sup>7-9</sup>



Figure 5.1 Localization of carbon black particles (1 % wt) in the PP phase of a PP/ PS blend (a), and at the interface between PP and PS in a similar blend (b)

This chapter presents results obtained using this approach for achieving morphology control in PLA/xGnP composites.

#### **Experimental details**

#### Materials

Injection molding grade polylactic acid, PLA 3001D, was obtained from Nature Works LLC (Minneapolis, MN) and used without purification. Poly(L-lactic acid), RESOMER<sup>®</sup> L210S, was purchased from Boehinger-Ingleheim Chemicals (Petersburg, VA). The intrinsic viscosity of this polymer sample is 3.8 dl/g for 0.1 % solution in chloroform at 25 °C). Exfoliated graphite nanoplatelets having an average size of 1  $\mu$ m (xGnP-1) was produced in-house from GrafGard<sup>TM</sup> 160\_50A acid intercalated graphite produced by Graftech (Cleveland, OH), as described in Chapter 2. Methylene chloride and 2-propanol were purchased from Sigma Aldrich. Polystyrene with weight average molecular weight 280,000 g/mol was purchased from Sigma Aldrich.

### Sample preparation

## a) Preparation of PLA 3001D/xGnP-1 composites

PLA composites with exfoliated graphite nanoplatelets (PLA 3001D/xGnP-1) were prepared by extrusion and injection molding, as described in the beginning of this chapter.

# b) Preparation of PLA L210S/xGnP-1 composites

PLA composites with exfoliated graphite nanoplatelets (PLA/xGnP-15 and PLA/xGnP-1) were prepared by solution mixing and compression molding, as described in the beginning of this chapter. The xGnP loading varied from 0 wt % to 30 wt %. The thickness of the composites was 0.13 - 0.20 mm.

# c) Preparation of PLA 210S/PS/xGnP-1 composites

Composites of xGnP-1 with a mixture of PLA L210S and PEG were prepared by solution mixing (in methylene chloride) and compression molding. xGnP-1 was dispersed in methylene chloride, PLA L2190S and PS were dissolved in methylene chloride, then the xGnP-1 dispersion and the polymer solution were mixed by ultrasonication as described before. The composite mixture obtained

after evaporation and drying overnight in a vacuum oven was compression molded under the same conditions as the PLA L210S/xGnP-1 composites.

# <u>Methods</u>

a) Guarded heat flow method for thermal conductivity determination

The thermal conductivity of PLA and its composites with xGnP-1, and xGnP-15 was measured using a UNITHERM<sup>™</sup> machine - UNITHERM<sup>™</sup> Model 2022 (Anter Corporation, Pittsburgh, PA). The tests were performed according to ASTM E1530 (Standard Test Method for Evaluating the Resistance to Thermal Transmission of Materials by the Guarded Heat Flow Meter Method Technique). Specimens of one inch diameter were cut from the compression molded samples using a punch. In order to ensure that the sample thickness was within the recommended range, 2 to 10 discs were stacked-up for the composites with higher xGnP loading. The samples were tested at 30 °C under an applied load of 30 psi. Reported results represent the average of three measurements for each xGnP loading.

b) Two-point method for evaluation of surface conductivity

Impedance Spectroscopy – two-point method – was employed to determine the resistivity of PLA/xGnP, PLA/PS/xGnP, and PLA/PEG/xGnP composites along the flow direction. Samples (approximately 0.13x5x12 mm) were cut from the center parts of compression molded films. The electrical resistance was measured in the frequency range from 0.1 to 100,000 Hz, as described in the first section of the present chapter. The reported results are average values for

measurements on five distinct samples for each xGnP-1 concentration in PLA, and represent bulk electrical conductivity (converted from resistance by taking into account the samples' dimensions).

# c) Dynamic mechanical analysis (DMA)

The storage moduli of PLA L210S, PS, and their composites with xGnP-1 and xGnP-15 were evaluated using a 2980 Dynamic Mechanical Analyzer (TA Instruments, New Castle, DE). The samples (approximately 5.50 mm x 16 mm x 0.10 mm) were cut from the compression molded films, and tested in tension during heating from room temperature to 120 °C. The reported values are for storage modulus at room temperature, and represent the average of three measurements per xGnP-1 concentration in the PLA, or PLA/PS blends.

# d) Hot stage optical microscopy

The samples for optical microscopy were prepared as thin polymer films by heating very thin sections of PLA/PS/xGnP-1 composites in a Mettler Toledo FP82 hot stage. Specifically, the polymer was placed on glass slide, covered with glass cover slip, and heated at a rate of 20 °C/minute from room temperature to 190 °C, kept isothermal for three minutes, then either allowed to crystallize upon cooling to room temperature. The morphology of PLA/PS/xGnP was observed using an Olympus BH2 optical microscope equipped with a Spot<sup>™</sup> camera.

#### Results and discussion

The maximum improvement (44.8 %) in thermal conductivity of extrusion mixed/injection molded PLA 3001D/xGnP-1 composites was obtained for 9 % wt xGnP-1 in the polylactide matrix (Figure 5.2). For these composites, the percolation threshold for electrical conductivity was also very high, at about 9 % wt (Figure 4.3).



Figure 5.2 Room temperature thermal conductivity of extrusion (melt) mixed injection molded PLA 3001D/xGnP-1 composites

Higher improvement in thermal conductivity was observed in the PLA L210S/xGnP-1 composites prepared by solution mixing and compression molding. This preparation method also allowed incorporation of much higher amounts of xGnP-1 in the polylactide matrix. For 30 % wt xGnP-1 (highest

loading), the improvement in thermal conductivity was as high as 300 % (Figure 5.3).



**Figure 5.3** Room temperature thermal conductivity of PLA L210S/xGnP composites prepared by solution mixing and compression molding

Figure 5.3 also shows that the improvement in thermal conductivity obtained for the 30 % wt xGnP-1 was achieved with approximately 15 % wt of the larger xGnP-15. The larger diameter nanoplatelets lowered the thermal contact resistance of the polymer/graphite interfacial surface to the total conductivity, as explained in Chapter 1 (Equation 1.1).

Apart from the xGnP particle size determining the extent of the contribution of the interfacial layer to the bulk thermal conductivity, it appeared that the PLA L210S/xGnP systems presented a percolating behavior for thermal conductivity, similar to the percolation behavior for electrical conductivity (Figure 5.4).



**Figure 5.4** Specific electrical conductivity of PLA L210S/xGnP-1 composites prepared by solution mixing and compression molding

Figure 5.4 shows the specific electrical conductivities of the same PLA L210S composites with xGnP-1 of two different sizes, and illustrates the similarity between the trends in thermal and electrical conductivities. These similarities, together with the results obtained for PLA 3001D/xGnP-1 composites, indicate a possible percolating mechanism for thermal conductivity, relying on the establishment of continuous xGnP network.

Both the electrical and the thermal conductivities of the composites improved when the amount and dispersion of xGnP in the matrix allowed contact between neighboring platelets. At high xGnP loadings, percolated networks in the semicrystalline PLA matrix could be created by the graphite nanoplatelets that were in excess for nucleation purposes and remained outside the newly formed crystallites. The percolation threshold for electrical conductivity was lower for the larger platelets, which were more likely to touch each other in the polymer matrix.

As expected, for the same amount of xGnP in the PLA matrix, the improvement in thermal conductivity was much smaller than the improvement in electrical conductivity.

We have previously shown<sup>10</sup> (Chapter 2) that amounts of xGnP-1 higher than 3 % wt determine dramatic decrease in the size of the polymer crystallites, and the polymer crystals nucleated by the graphite nanoplatelets are more irregular. Unlike during electric transport – when electrons travel through the percolating tube network – during heat transfer the thermal energy flow always involves the polymer matrix. The irregular crystalline structure generated by the presence of higher amounts of xGnP does not affect the electrical conductivity as long as a continuous path is formed by the nanoplatelets, but is not beneficial for achieving high thermal conductivity.

The possibility of a percolation threshold for thermal conductivity was intriguing, since previous studies on polymer/CNT composites indicate that thermal conductivity does not show a clear percolation.<sup>4, 11</sup>

As described in the introduction to this chapter, the heat transfer in polymer/CNT composites is governed by the relatively small contrast between the thermal conductivity of the matrix and that of the nanotubes. Numerical simulations<sup>4</sup> indicated that if the contrast between thermal conductivity of the matrix and thermal conductivity of the CNT increases by a factor of 1000, the heat flux at contact increases by two orders of magnitude. Even sharper relative

increases were predicted for larger thermal conductivity ratios, and strong percolation threshold in conductive transport was predicted. Our results indicate that the either the contrast between the thermal conductivity of exfoliated graphite nanoplatelets and the thermal conductivity of the PLA is higher than the expected 10<sup>4</sup>, or the interfacial thermal resistances plays a more important role as the xGnP loadings increase. The above-mentioned simulation results indicate that in order to achieve a percolation threshold for thermal conductivity, the difference between the thermal conductivity of the polymer and that of the nanoplatelets should be of the order of 10<sup>7</sup>. Such a high contrast is not very probable since the thermal conductivity of the PLA matrix is about 0.20 W/mK, and the conductivity of xGnP cannot be exceeding the thermal conductivity of individual graphene sheets.<sup>1</sup> We believe that the interfacial thermal resistance between graphite nanoplatelets is lower than the polymer-xGnP interfacial heat resistance, and the more nanoplatelets in contact with each other, the higher the conductivity of the composite. Larger improvement in thermal conductivity was not achieved because as the amount of xGnP was large enough to allow continuous contact between nanoplatelets, the crystalline structure of the polymer matrix interfered with the ability of the platelets to form a conductive path. When xGnP-1 was dispersed in immiscible PLA/PS blends, the phase separation between PLA and PS directed the xGnP towards forming a continuous path (Figure 5.5).



Figure 5.5 Optical micrographs of a) PLA L210S containing 10 % xGnP-1 and b) composite sample containing 70 % PLA L210S, 20 % PS, and 10 % xGnP-1

The thermal conductivity of PLA/PS/xGnP-1 systems showed the potential of the polymer blend to lead to better thermal transfer. As shown in Figure 5.6, the thermal conductivity of PLA is approximately 0.20 W/mK, PS has a lower conductivity of 0.13 W/mK (due to its amorphous nature), while a mixture of 90 % wt PLA and 10 % wt PS has intermediate thermal conductivity of 0.17 W/mK. Addition of xGnP-1 to the PLA/PS blends helps improving the thermal conductivity. For example (Figure 2.6.10), PLA containing 10 % xGnP-1 is less conductive than a composite containing 80 % PLA, 10 % PS, and 10 % xGnP-1. The same trend can be seen for composites containing 20 % xGnP-1.



Figure 5.6 Thermal conductivity of PLA/PS/xGnP-1 composites

The results obtained for the thermal conductivity of PLA/PS/xGnP-1 composites show that taking advantage of preferential localization of xGnP in a blend of immiscible polymers can lead to improvement in thermal conductivity. However, for PLA/PS systems analyzed, this approach is in the detriment of the mechanical properties. Figure 5.7 shows that the modulus of the polylactides used in these experiments is 3.19 GPa, and the modulus of PS is 2.69 GPa. The modulus of PLA samples containing 1 % wt xGnP-1 is 30 % higher than that of pure PLA. PLA containing 1 % wt xGnP-1 and increasing amounts of PS show a decrease in modulus for 10 %, 20 %, and 30 % wt PS. The modulus of PLA/PS blends containing 1 % xGnP-1 increases again after phase inversion, when the system starts to be dominated by the PS.



Figure 5.7 Storage moduli of PLA, PS, and PLA/PS/xGnP-1 composites containing 1 % xGnP-1

#### Conclusions

Exfoliated graphite nanoplatelets can impart thermal conductivity to PLA. The improvement was as high as 300 % for 30 % xGnP-1 in PLA L210S, and over 500 % for 15 % xGnP-15 in the same matrix. The results indicate that the improvement in thermal conductivity is limited by the interfacial heat transfer between the polymer and the graphite nanoplatelets. Larger graphite nanoplatelets are more efficient in improving thermal conductivity, as the contribution of the polymer/graphite interfacial layer to thermal conductivity is inversely proportional to the size of the platelets.

As the amount of xGnP in the PLA matrix increases, regardless of platelets size, the nucleating effect of xGnP on the PLA determines the rapid formation of crystalline structures that are more numerous and more irregular, increasing the overall disorder in the polymer matrix, which limits the improvement in thermal conductivity.

Better improvement in thermal conductivity could be achieved by using biphasic polymer blends, by directing the graphite nanoplatelets either in one of the polymers, or at the interface between the immiscible polymers. In the PLA/PS system studied, the improvement in thermal conductivity was in the detriment of mechanical properties, which showed a typical phase inversion behavior, as the system was dominated either by the semicrystalline PLA, or by the amorphous PS.

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## **CHAPTER 6**

# SCANNING PROBE THERMAL ANALYSIS OF POLYLACTIC ACID/ EXFOLIATED GRAPHITE NANOPLATELET NANOCOMPOSITES

Scanning probe thermal analysis, also known as nanoscale thermal analysis (nano-TA), is introduced here as an important nanoscale characterization tool for PNC. The technique was used in this research for the analysis of the nanoscale structure of PLA/xGnP nanocomposites. The first part of this chapter presents the investigation of calibration standards to be used for the analysis of polymer nanocomposites in which the polymer matrix melts under 200 °C, and experiments conducted to determine the effect of heating rates on the measured melting temperature of a variety of polymers. The second part, which constitutes work published in 2008<sup>1</sup> in Journal of Biobased Materials and Bioenergy, presents the use of nano-TA together with conventional thermomechanical analyses to offer insight on the effect of xGnP on the crystallization behavior of PLA, and to explore the relationship between the polymer's molecular weight and the dispersion of xGnP in the matrix. Specifically, the technique was used to monitor cold crystallization phenomena, and to assess the dispersion of nano-size fillers in the polymer matrix.

# Calibration standards and testing conditions for the study of PHB/xGnP and PLA/xGnP nanocomposites

### Introduction

Nano-TA is a local thermal analysis technique utilizing a novel micromachined scanning probe microscopy tip with an integrated heater to monitor thermal behavior of materials at nanoscale dimensions. The measurements consist in positioning the tip at a fixed location, increasing the tip temperature and monitor the deflection, to detect transitions such as melting temperature ( $T_m$ ) and glass transition temperature ( $T_g$ ).

The spatial resolution for imaging with this system is reported to be one hundred times better than its predecessor, micro-TA ( $\mu$ TA), primarily due to advances in probe technology. The new probes have increased tip height and sharpness, enhanced cantilever geometry for laser alignment and relatively low spring constants, which are important features for imaging soft materials such as polymers in the contact mode without causing significant damage to the surface of the specimen.

For polymers and PNC, while DSC gives quantitative information regarding the dependence of the degree of crystallinity on cooling rates, nano-TA offers the unique advantages of *in-situ* observation of the polymer's morphology under the same conditions, providing valuable information for practical applications.

A special nano-TA probe containing an embedded miniature heater is used *in lieu* of the conventional AFM probe (see Figure 6.1 a).



Figure 6.1 Scanning Electron Micrographs of a first generation nano-TA probe showing a) entire cantilever; b) the 1μm tip) and c) a temperature map of the probe (Images courtesy of Anasys Instruments, CA)

Figure 6.2 shows representative AFM images of a PLA test area before and after nano-TA. These images attest to the high quality of surface characterization obtainable with the nano-TA probe.



Figure 6.2 AFM images of a PLA surface before nano-TA a) height image, and b) deflection image and c) after nano-TA, showing the indentation formed when the sample melts (Scans are all 3  $\mu$ m<sup>2</sup> and collected at a scan rate of 2 Hz.)

Figure 6.2 shows details of the morphology of the PLA sample. Although it appears that an area of approximately 2  $\mu$ m<sup>2</sup> was affected by the nano-TA measurement, the actual size of the indent is on the order of a couple hundred nanometers. The area shown in Figure 6.2b is larger due to polymer that recrystallized after the tip was withdrawn, and the region was brought back to room temperature.

This type of probe stems from the work of Dinwiddie *et al.*,<sup>2</sup> who combined thermal conductivity measurements with AFM mapping topography. Others have since contributed to this technology.<sup>3-6</sup> Together with specially designed hardware and software, it is possible to obtain nanoscale resolution of a material's surface using either contact or tapping mode AFM, while simultaneously applying heat locally through the probe tip for thermo-mechanical investigations. The nano-TA measurement is analogous to TMA, which records changes in the physical dimensions of a sample as a function of temperature and/or time.

Nano-TA data of cantilever deflection as a function of probe tip temperature for PHB is shown in Figure 6.3. The initial upward deflection of the probe cantilever is the results of the thermal expansion of the sample and the sudden sharp downward deflection is indicative of the melting transition.



Figure 6.3 Example of nano-TA thermal profile for PHB

Unlike pure elements, which have a well defined melting temperature, polymers melt over a broad temperature range. Polymer melt profiles are routinely measured using DSC and the melt temperature is typically assigned as the peak temperature of the endothermic melting event. Due to molecular weight distribution considerations, crystalline structure and size effects, the onset of melting generally occurs well before the peak endothermic temperature. Consequently, it is often useful to define the extrapolated onset melting temperature as the point where the baseline intersects the tangent through the linear section of the first order endothermic event before the peak temperature is attained. The difference between the temperature corresponding to the extrapolated onset of the melting transition and the temperature of peak recorded for the melting endotherm can be substantial. As is the case with differential scanning calorimeters, the nano-TA unit requires detailed temperature calibration procedures using known standards, as well as an understanding of the precision of the temperature measurement. Since the technique is new, it was imperative to evaluate calibration standards that would allow accurate measurements within the desired temperature range. The focus of this work being nanocomposites from PHB and PLA, the desired temperature range was room temperature to 200 °C (~ 20 °C above the melting temperature of each of the polymer matrices).

A good calibration standard should have a number of desirable properties, such as a well-documented melting temperature, availability in a suitable form for analysis, homogeneity, stability, low toxicity, and traceability to a national reference laboratory.<sup>7</sup> The calibration standards used for micro-TA are polymeric materials since these do not interact with the platinum sensor of the micro-TA probe. It is also essential to use pure, crystalline polymers with a single polymorphic form.

PCL, PE, and PET possess the requisite properties to serve as standards for calibrating the temperature response of the nano-TA probe. Pro-fax 6301, a PP homopolymer, was also investigated for the use as calibration standard.

The effect of heating rates on polymeric thermal melt behavior was assessed using the nano-TA instrument at ramp rates from 60 to 600 °C per minute.

# Experimental details

### **Materials**

Poly( $\xi$ -caprolactone), polyethylene, and poly(ethylene terephthalate calibration standards were provided by Anasys Instruments, CA and used as received. Pro-fax 6301 was obtained from Basell Polyolefins and was used without further purification.

### Sample preparation

PCL, PE, and PET calibration standards were used as received. Thin films of Pro-fax 6301 were obtained in a Mettler Toledo FP82 hot stage by heating at 20 °C/min a small amount of polymer sandwiched between a glass slide and a cover slip. These samples were obtained after nonisothermal crystallization upon cooling ~20 °C/min to room temperature from 190 °C. To ensure complete melting, the samples were held isothermally above 190°C for five minutes.

## **Methods**

# a) Differential scanning calorimetry

DSC measurements were made using a 2920 DSC (TA Instruments, New Castle, DE) operated in the standard mode with a nitrogen gas purge. The unit was calibrated using an Indium standard. For each run, a fresh sample (5-10 mg) of polymer was encapsulated in crimped aluminum pans. Three different samples were tested for each polymer. Samples were tested at a heating rate of
10 °C/min from room temperature to 100 °C, 150 °C, 280 °C, and 250 °C respectively.

The extrapolated onset temperature,  $T_{mo}$ , was assigned by the intersection of a tangent constructed to the baseline with a tangent through the linear portion of the first order melt transition. The manufacturer's software was employed to construct the tangents for determination of the extrapolated onset melting point,  $T_{mp}$ .. The peak melt temperature was determined by using the vendor's software tools to locate the temperature where the material was at its peak endothermic response.

#### b) Scanning probe thermal analysis

Tests were performed using a nano-TA instrument (Anasys Instruments, CA) in conjunction with a Nanoscope IV (Veeco Instruments, CA) scanning probe microscope. A silicon micromachined thermal probe, with a cantilever thickness of approximately 2  $\mu$ m and having a resistivity of about 1 k $\Omega$  was used for all the tests. Heating was made possible through a high resistance region within the probe, and controlled by varying the voltage applied through the nano-TA electronics. The maximum temperature attainable for this particular probe was approximately 250 °C. The probe temperature was initially calibrated with PCL (60 °C), PE (130 °C), and PET (238 °C). AFM imaging was done in the contact mode at a scan rate of 2 Hz for scan sizes of 3  $\mu$ m<sup>2</sup> to locate and select an appropriate area of the surface for nano-TA testing.

#### PCL, PE and PET as calibration standards

The DSC results for PCL, PE, and PET are presented in Table 6.1 and Figure 6.4. For PCL and PE, the  $T_{mp}$  values determined by DSC were in close agreement with the literature melting temperatures,  $T_m$ (lit). However, for PET, the  $T_{mo}$  was in better agreement with the  $T_m$ (lit) value. The  $T_{mp}$  of PET from DSC was measured to be ~17 °C higher than the  $T_m$  (lit) although the cause for this discrepancy is not known.

The nano-TA melt temperatures for PCL and PET (Table 6.1) closely correspond to the  $T_{mo}$  values determined by the DSC. This was not the case for PE, which showed a large variability in the nano-TA results compared to the other polymers used as calibration standards.

Literature Nano-TA Sample DSC value *T<sub>mo,</sub>* [°C] T<sub>mp</sub> [°C] T<sub>m</sub> [°C] T<sub>m</sub> (lit) [°C] PCL PCL1 54.27 62.01 55.26 PCL2 54.69 61.53 56.41 60 PCL3 54.94 61.73 55.84 54.63 61.76 55.82 Average PCL 0.34 0.24 0.60 Stdev. -PE PE1 117.99 130.04 126.95 PE2 115.53 129.40 138.04 130 130.26 PE3 118.33 140.41 117.28 Average 129.50 135.14 PE Stdev. 1.53 0.45 7.19 -PET PET1 238.03 256.91 235.56 PET2 236.01 253.84 230.42 238 PET3 232.37 253.94 235.83 235.47 254.90 233.94 Average PET 2.87 1.74 3.05 Stdev. -Pro-fax 147.58 162.61 Pro-fax1 142.21 147.84 163.23 139.54 Pro-fax2 160 Pro-fax3 147.92 162.81 142.54 147.78 162.88 141.43 Average Pro-fax 0.18 0.32 1.65

#### Melting temperatures of PCL, PE, PET and Pro-fax 6301 obtained Table 6.1 from DSC and nano-TA experiments

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**Figure 6.4** DSC curves showing the melting behavior of a) PCL; b) PE and c) PET

Figure 6.5 shows a summary of the  $T_{mo}$ ,  $T_{mp}$ ,  $T_m(lit)$ , and  $T_m$  for the three calibration standards. It should be noted that the standard deviations of the  $T_{mo}$ and  $T_{mp}$  values obtained by DSC were smaller for PCL, followed by PE, then PET. Except for PE, the standard deviations calculated from the nano-TA results were comparable with those for DSC data collected on the same material. This indicates that nano-TA has the potential of being used as an effective thermal characterization tool, leading to reproducible results comparable to a widely-used and accepted calorimetric technique. The exact cause of the variability of the nano-TA results on PE was not determined, but generally the inherent characteristics of polymer samples (e.g. degree of crystallinity, molecular weight distribution), or even the variability in the response of the nano-TA probe as a function of temperature, should be considered as contributing factors. Additionally, it must be considered that properties of surfaces may be dissimilar to the bulk properties of a material. The ability to measure melt properties with nano-TA may not reflect the bulk material properties. Based on these results, Pro-fax 6301 was investigated as an alternative calibration standard to PE. Both the DSC and the nano-TA results for this material were very reproducible, showing small standard deviations (Table 6.1). Hence, Pro-fax 6301 has suitable thermal behavior to be a viable standard for nano-TA calibration.



Figure 6.5 Summary of DSC results showing T<sub>mo</sub>, T<sub>mp</sub>, T<sub>m</sub>(*lit*), and T<sub>m</sub>(nTA) values for PCL, PE, PET and Pro-fax

#### Nano-TA heating rate effects on polymer melt behavior

The effect of nano-TA heating rate on the melt behavior of Profax 6301, PE, PHB, and PET was evaluated at temperature ramp rates of 60 to 600 °C/min. The tip was placed on a random location on the surface and three tests were performed for each heating rate. As soon as the melting transition was observed, the tip was quickly withdrawn from the surface.

The nano-TA heating rate data are presented in Figure 6.6 and Table 6.2. The  $T_m$  values show good reproducibility, and the melting transitions are obvious. In general, the  $T_m$  values were not significantly affected by the heating rate, allowing for reproducible results even for scan rates as high as 600 °C/min. It was observed that as heating rates increased, the sharpness of the melting transitions decreased slightly The rates of thermal expansion, as reflected in the slope of cantilever deflection versus temperature curve, were also observed to be slightly higher for slow heating rates (10 and 20 °C/min) compared to faster rates (> 30 °C/min). At slower ramp rates, the probe is in contact with the sample for longer time periods, giving more time for the sample to undergo thermal expansion compared to faster heating rates.

Heating Rate	$T_m$ (Nano-TA) (°C)									
(°C/min)	PE	PET	Pro-fax							
60	129.6	226.3	140.8							
120	130.0	228.4	140.2							
180	135.1	231.7	140.9							
240	128.2	230.1	141.8							
300	133.6	229.0	143.6							
360	129.4	228.7	140.2							
420	130.5	226.8	139.6							
480	130.7	227.6	141.6							
540	132.1	228.1	144.4							
600	126.4	226.2	140.2							

Table 6.2Melting temperatures recorded by nano-TA using scan rates from<br/>60 to 600 °C/min



Figure 6.6 Nano-TA results showing the effect of heating rate on the melt temperature for a) Pro-fax 6301, b) PE and c) PET

# Conclusions

PCL, PE, and PET were proved to be efficient calibration standards for nano-TA experiments requiring heating up to 200 °C. The results of this study are important since nano-TA is not an established method for investigation of PNC and a good understanding of the method's advantages and limitations is requires for before subsequent use in nanoscale characterizations.

When used in conjunction with AFM, nano-TA can provide thermal data related to localized areas of a sample. In this respect, nano-TA provides information specific to the surfaces of materials on the nanoscale which are not obtainable by bulk investigation methods such as DSC. Nano-TA can measure melt temperatures  $(T_m)$  of polymers at very fast heating rates. In this study, varying the heating rate from 60 to 600 °C/min gave consistent and reproducible identification of the melting points, gualifying nano-TA as a viable method to measure the melt temperature of many polymeric materials. However, it should be noted that heat loss still occurs both within the probe and to the atmosphere. It is difficult to ascertain the extent of this loss, and also difficult to determine how this affects the  $T_m$  values measured. The standard deviations of  $T_m$  values obtained via nano-TA were always larger compared to the corresponding values from DSC measurements, but this variability may be due in part to local surface properties of the materials such as roughness, as well as atmospheric conditions like humidity.

Finally, a note of caution was raised regarding potential artifacts resulting from sample preparation. Since the nano-TA interacts with only the first few

nanometers of the sample surface, consistent methods of sample preparation must be applied in order to insure that the results are representative of the sample and not a local artifact resulting from surface preparation.

# Experimental investigation of PLA/xGnP

#### Introduction

Scanning probe thermal analysis was further employed for the investigation of PLA/xGnP-1 nanocomposites prepared by solution mixing and compression molding. This preparation technique was shown (Chapter 4) to lead to the best dispersion of xGnP-1 in the polylactides matrices. The purposes of the nanoscale investigations presented here were to relate modifications in polymers' morphology induced by the xGnP to changes in the mechanical properties of the composites, and to establish if the high nucleating effect of xGnP is a limiting factor in improving the properties of resultant nanocomposites.

#### Experimental details

## <u>Materials</u>

Poly(L-lactic acid) was purchased from Boehinger-Ingleheim Chemicals (Petersburg, VA). Two different molecular weight PLA samples were used in this

study: RESOMER<sup>®</sup> L209S (intrinsic viscosity 3.0 dl/g for 0.1 % solution in chloroform at 25 °C), and RESOMER<sup>®</sup> L210S (intrinsic viscosity 3.8 dl/g for 0.1 % solution in chloroform at 25 °C). Methylene chloride and 2-propanol were purchased from Sigma Aldrich. Exfoliated graphite nanoplatelets having an average size of 1  $\mu$ m (xGnP-1) was produced in-house from GraphGuard<sup>TM</sup> 160-50A acid intercalated graphite produced by Graftech (Cleveland, OH), as described in Chapter 2.

#### Preparation of PLA/xGnP-1 composites

PLA composites with xGnP-1 were prepared by solution mixing and compression molding. The xGnP-1 loading varied from 0 wt % to 9 wt % for both PLA samples (L209S and 210S). For each xGnP-1 loading, 1 g of PLA/xGnP-1 mixture was prepared as follows: appropriate amounts of xGnP-1 were dispersed in 20 mL methylene chloride by sonication (5 min, 10 W) using a VirSonic 100 Cell Disrupter from Virtis (Gardiner, NY). Corresponding amounts of PLA were further dissolved in the xGnP-1/ methylene chloride dispersions, and the obtained PLA/xGnP-1 mixtures were precipitated using 2-propanol. The resulted PLA/xGnP-1 materials were kept at room temperature overnight, and then dried in a vacuum oven at 80 °C for 20 h to ensure the complete evaporation of the organic solvents. The dried PLA/xGnP-1 mixtures were compression molded at 200 °C for 2 min, under an applied pressure of 18,000 psi, using a Carver laboratory press (Carver Inc., Wabash, IN). The press' platens were pre-heated to 200 °C prior to compression molding.

#### <u>Methods</u>

a) Dynamic Mechanical Analysis

The storage moduli of PLA, and PLA/xGnP-1 composites were evaluated using a 2980 Dynamic Mechanical Analyzer (TA Instruments, New Castle, DE). The samples (approximately 5.50 mm x 16 mm x 0.10 mm) were cut from the compression molded films, and tested in tension during heating from room temperature to 120 °C. The reported values are for storage modulus at room temperature, and represent the average of three measurements per xGnP-1 concentration in the PLA.

#### b) Differential Scanning Calorimetry

The melting and crystallization behavior of PLA and PLA/xGnP-1 composites were investigated using a using a 2920 Modulated DSC (TA Instruments, New Castle, DE). The runs were performed under nitrogen flow, after calibrating the DSC instrument using an Indium standard. For each run, a fresh sample (6-10 mg) of polymer/ composite was placed in a seal aluminum pan and subjected to two heating/ cooling cycles. During the first cycle, incorporated in the DSC method to ensure the erasure of samples' thermal history, the samples were heated (10 °C/min) from room temperature to 200 °C, kept isothermal at 200 °C for 10 min, cooled (10 °C/min) to 0 °C, and equilibrated at 0 °C. The second heating/cooling cycle immediately followed and involved heating (3 °C/min) to 200 °C, keeping the samples isothermal at 200 °C, then cooling (3 °C) to room temperature. Except for the data in Figure 5, where the first heating cycle was

presented, all data reported and analyzed refer to the second heating/ cooling cycle.

#### c) Optical microscopy

The samples for optical microscopy were prepared as thin polymer films by heating very thin sections of PLA/xGnP-1 compression molded composites in a Mettler Toledo FP82 hot stage. The polymers were placed on glass slides, covered with glass cover slips, and heated at a rate of 10 °C/minute from room temperature to 200 °C, kept isothermal for ten minutes, then allowed to crystallize upon cooling to room temperature. The morphology of PLA and the size of the spherulites were observed using an Olympus BH2 optical microscope equipped with a Spot<sup>™</sup> camera.

# d) Scanning probe thermal analysis

The tests were performed using a nano-TA instrument (Anasys Instruments, CA) in conjunction with a Nanoscope<sup>TM</sup> IV instrument (Veeco, Santa Barbara, CA) equipped with a *J* scanner, as described in the first part of this chapter. The maximum temperature attainable for this particular probe was approximately 250 °C. The probe temperature was initially calibrated using polymer standards: poly( $\varepsilon$ -caprolactone) (m.p. 60 °C), polyethylene (m.p. 130 °C), and polyethylene terephthalate (m.p.238 °C), as described in the previous section.

The tested surfaces were sections of the compression molded composite films prepared as described above. In order to select areas on the surfaces that

were appropriate for the nano-TA testing, initial 3  $\mu$ m<sup>2</sup> scans were collected in contact mode without heating the probe, using a 3 Hz scan rate. The scan size was reduced to 1 nm<sup>2</sup>, and the probe was heated at a rate of 10 °C/sec from 25 °C to an end temperature of 180 °C. For all the tests, the delay was 0.1 sec, the hold time was 0.1 sec, and the probe cooling rate was 20 °C/min. Data were collected at a rate of five readings per second, and the reported results represent the average of five measurements per composite sample.

#### **Results and discussion**

# Mechanical properties of PLA/xGnP composites

The storage moduli of PLA L210S/xGnP-1 composites, as determined by DMA, increased with increasing amounts of xGnP-1 in the polymer matrix. The improvement was consistently greater than 50-60 % for 3-9 % wt xGnP-1 in PLA L210S. The same amounts of xGnP-1 did not lead to similar improvement of the storage modulus when incorporated in the lower molecular weight polylactic acid, PLA L209S (Figure 6.7). In the PLA L209S composites, the storage modulus improvement was greater than 50 % only for composites with 6-7 wt % xGnP.



Figure 6.7 Storage moduli of PLA/ xGnP-1 composites

#### Crystallization of PLA/xGnP composites

Polylactides are semicrystalline polymers, and their mechanical properties, as well as the mechanical properties of the composites for which they serve as matrices, are expected to depend on crystallinity and morphology. Since the composite samples were prepared using compression molding, a dynamic processing method, the nonisothermal crystallization from the melt was analyzed in order to elucidate the differences observed in storage moduli. The DSC analysis of PLA L209S, PLA L210S, and their composites with xGnP-1 revealed that the crystallization behavior of both PLA samples was significantly affected by xGnP-1. Low amounts of xGnP-1 (up to 1 % wt) lead to increased melt crystallization temperatures (Figure 6.8, and Table 1), which indicated a nucleating effect of the nanoplatelets, similar to the nucleating effect observed recently in PHB/xGnP-1, and PP/xGnP-1 composites<sup>9:10</sup>. The nonisothermal

crystallization peaks for PLA L209S and PLA L210S containing 0.01 % wt xGnP-1 were narrower than the peaks recorded for the neat polymer samples, which indicated that the crystallization process was faster in the presence of xGnP-1.



Figure 6.8 DSC analysis of the nonisothermal crystallization from the melt of (a) PLA L209S and (b) PLA 210S and their composites with xGnP-1

Summary of DSC analysis of melting and nonisothermal crystallization from the melt of PLA/xGnP-1 composites Table 6.3

×	(%)		35.53	40.51	34.99	38.89	36.21	37.61	38.38	36.99	33.90	38.27	37.32		11.82	36.73	36.40	33.60	33.44	34.61	31.15	33.25	36.01	35.94	35.73
DHœ		,	38.73	44.15	37.76	41.54	38.29	39.35	39.74	37.9	34.36	38.38	37.02		12.88	40.03	39.28	35.89	35.36	36.22	32.26	34.07	36.50	36.04	35.44
$T_{cc}$	(c))	P-1	109.08; 119.11	125.23	106.38; 124.35	110.23; 127.59	111.25; 125.33	111.49; 125.63	112.49; 126.82	115.66	112.42; 124.15	115.14; 127.41	111.27	1P-1	104.05	123.49	122.87	121.99; 110.71	115.86	119.78	109.88; 120.00	111.12; 122.07	121.12	123.37	113.2; 123.85
DH <sub>m</sub>		L209S/xGi	42.91	40.21	44.36	44.96	40.36	43.74	40.39	41.17	36.7	41.12	39.34	L210S/xGr	41.64	36.21	28.78	32.04	36.16	37.05	32.4	34.3	38.52	36.01	38.49
$\mathcal{T}_m$	(°°)	PLA	180.19	179.25; 182.45	178.95	178.81	178.74; 181.09	181.4	181.49	177.27; 182.26	177.47; 181.59	178.61; 181.9	181.33	PLA	179.68	178.74	178.92	179.22; 181.32	178.2; 181.83	178.68; 181.21	181.02; 181.02	178.86; 181.21	177.9; 182.64	179.71; 182.78	178.04; 181.98
$T_{mo}$	(၁°)		173.13	173.64	173.68	174.21	173.21	172.96	172.39	172.63	174.12	172.34	173.8		173.37	175.52	176.07	173.39	172.83	173.8	173.43	174.34	173.68	175.26	172.66
$T_{a}$	(၁့)		67.76	61.89	61.39	63.93	66.17	62.69	64.51	62.86	63.49	62.89	64.50		65.66	64.58	64.15	64.4	65.94	62.67	63.16	65.83	63.69	65.15	63.49
xGnP-1	(% wt)		0	0.01	1	2	с С	4	5	9	7	æ	6		0	0.01	1	2	n	4	S	9	7	8	ი

In nanocomposites containing xGnP<sup>8, 9,</sup> narrower crystallization peaks were also correlated with smaller crystallites formed by the polymers in the presence of xGnP-1, as shown also in Chapter 2 of this dissertation.

Figure 6.9 shows an example of the effect of xGnP-1 on the size of the crystalline structures formed by PLA L210S with nonisothermal cooling from the melt. The neat PLA forms spherulitic structures 20 – 100  $\mu$ m in diameter (Figure 6.9,a). The addition of 0.01 % wt xGnP-1 lead to formation of much smaller crystalline structures (Figure 6.9,b), while crystalline structures were not detectable using optical microscopy when the amounts of xGnP-1 exceeded 1 wt %. Similar nucleating effects of nanosize reinforcements, leading to higher temperatures of crystallization from the melt, and reduction in spherulitic size, were reported for polylactic nanocomposites with carbon nanotubes<sup>10, 11</sup>, and layered silicates.<sup>10</sup> Similar crystallization behavior was reported for nanocomposites obtained from other nanocomposites of semicrystalline nylon-6/clay<sup>12</sup>, polypropylene/clay<sup>13</sup>, polymers, such as and polypropylene/carbon nanotubes. 14, 15

For 1 % wt xGnP-1, a clear difference was observed between PLA L209S and PLA L210S: for the low molecular weight PLA sample, a bimodal nonisothermal crystallization curve was observed, which could be related to dispersion issues leading to hindrance of crystal growth.<sup>16, 17</sup>



Figure 6.9 Optical micrographs showing spherulites of (a) pure PLA L210S; (b) PLA L210S/ 0.01 % % wt xGnP-1 and (c) PLA L210S/ 5 % wt xGnP-1 formed during nonisothermal crystallization from the mett. The scale bar is 20 µm.

No significant differences in the mett crystallization behavior were observed between the composites of the two different molecular weight polylactides containing amounts of xGnP-1 higher than 1 % wt. The melt crystallization peaks recorded for composites containing more than 1 % wt xGnP-1 were wider and occurred at lower temperatures than the peaks recorded for low amounts of xGnP-1, regardless of polymer's molecular weight. Bimodal crystallization curves were further observed for increased amounts of xGnP-1 in both matrices, indicating possible agglomeration of the platelets and creation of polymer-rich regions. The polylactides crystallized heterogeneously, at higher rates, in the vicinity of xGnP-1, while in the polymer-reach regions, the crystallization was homogeneous and similar to the neat polymers'.

The DSC analysis of neat PLA L209S and PLA 210S samples also revealed that the neat polymers undergo cold crystallization, upon heating from room temperature. The cold crystallization peak temperatures were recorded between 93 - 106 °C (Table 6.4), depending on the heating rate, as will be discussed further in this paper. The DSC analysis did not detect cold crystallization after addition of xGnP-1 to either one of the polymer matrices.

T<sub>icc</sub> (°C)  $T_{cc}(^{\circ}C)$  $\Delta H_{cc}$  (°C) Heating 3 5 10 3 5 10 3 5 10 rate (°C/min) **PLA L209S** Test 1 87.92 89.61 95.65 94.27 98.61 105.03 22.46 27.15 28.88 Test 2 86.04 91.19 93.36 94.27 99.07 105.16 23.47 27.05 27.10 24.87 22.78 Test 3 88.12 89.17 93.60 94.52 98.58 104.03 27.46 Average 87.36 89.99 94.20 94.35 98.75 104.74 23.60 25.66 27.81 Standard 0.94 0.22 0.87 1.03 0.12 0.50 0.99 2.04 0.77 deviation **PLA L210S** Test 1 82.62 88.42 93.43 95.26 7.231 80.62 102.94 11.31 13.75 97.17 Test 2 81.89 86.01 89.98 94.10 104.24 14.31 16.61 17.30 92.24 Test 3 85.70 83.93 94.82 96.60 103.06 12.03 13.00 9.836 103.41 82.74 84.19 90.21 94.12 96.34 11.19 13.64 13.63 Average Standard 2.16 1.40 1.57 0.57 0.80 0.59 2.95 2.21 3.05 deviation

Table 6.4Summary of the DSC analysis of cold crystallization of PLA L209S<br/>and PLA L210S for different heating rates

#### Melting of PLA/xGnP composites

The DSC analysis indicated that neat PLA L209S and PLA L210S melt at 179-180 °C (Table 6.3). For both polymer composites with xGnP-1, bimodal melting peaks were recorded. Additional peaks (shoulders) were observed at 181-182 °C in the samples containing xGnP-1. The higher temperature peaks were attributed to polymer regions entrapped between graphite nanoplatelets, which retard the melting transition.

The melting behavior of PLA/xGnP-1 composites was further analyzed using scanning probe thermal analysis in order to investigate possible connections between agglomeration of xGnP and polymer molecular weight which were not evidenced by the DSC analysis. For the neat PLA L209S and PLA L210S, the deflection versus temperature curves were M-shaped: the tip deflection increased upon heating from room temperature to approximately 80 °C, decreased until the tip temperature reached approximately 100 °C, then increased again until the onset of melting transition ( $T_{mo}$ ) (Figure 6.10). Scanning probe thermal analysis revealed three major differences in the melting behavior of the different molecular weight PLA and their composites with xGnP-1.

The recorded  $T_{mo}$  was lower (~ 150 °C) for PLA L209S than for PLA L210S (~159 °C). Lower temperatures were also recorded for the onset of melting transition of PLA L2109S/xGnP-1 composites than for the PLA L210S/xGnP-1 counterparts.

The deflection curves for PLA L209S/ xGnP-1 composites were *M*-shaped, similar to the curves recorded for the neat polymer (Figure 6.10a). The deflection *versus* temperature curve for PLA L210S was also *M*-shaped (Figure 6.10b), but linear increases of deflection with temperature were recorded for the majority of the PLA L210S samples containing xGnP-1.



Figure 6.10 Scanning probe thermal analysis deflection curves for a) PLA L210S/xGnP-1 and b) PLA L209S/xGnP-1 composites

For all the PLA L209S/ xGnP-1 composites, the deflections recorded were lower than the deflection measured for the neat PLA L210S (Figure 6.10a), while higher deflections were recorded for all PLA L210S/xGnP-1 composites than for the neat PLA L209S.

There appear to be three possible explanations for the differences in melting behavior. First, differences in xGnP-1 dispersion in the two PLA matrices of different molecular weight were considered to be responsible for the composites behavior when subjected to nanoscale thermal analysis. Second, the extremely high heating rate employed during scanning probe thermal analysis was suspected to have enabled the identification of polymer chain re-arrangements that were not detectable by conventional thermal analysis (DSC). Third, differences in thermal conductivities of PLA L209S/xGnP-1 and PLA L210S/xGnP-1 were explored since tip deflection depends on the thermal and electrical properties of the surface. This hypothesis is currently under consideration.

The possibility of different dispersion of xGnP-1 in the two molecular weight PLA samples was also indicated by thermomechanical analysis (DSC and DMA). DMA results, in particular, indicated a smaller extent of improvement in storage modulus in the case of composites prepared with the lower molecular weight polymer. It is likely that xGnP-1 dispersed better in PLA L210S, which was better nucleated by the nanoplatelets, generating more polymer crystallites and fewer regions in which xGnP-1 agglomerated. Dispersion is a key issue in processing polymer nanocomposites, and has a strong impact on mechanical properties. As opposed to phase separation – occurring when incorporating micro-size fillers in polymers –, as the size of the fillers in the polymer matrices decreases, dispersion and agglomeration become the important problems to be overcome when attempting to obtain high-performance polymer composites.<sup>18</sup>

In the PLA/xGnP-1 systems studied, more uniform crystalline structures would lead to higher probabilities that the nano-TA tip encounters polymer

spherulites rather than regions where xGnP-1 agglomerates. The tip deflection would be expected to be higher for polymer-rich regions.

Scanning probe thermal analysis is a surface technique, essentially different from DSC, which is a bulk characterization method. Besides this important difference, the heating rates used by the two techniques are significantly different. The DSC runs investigating melting and crystallization were conducted at heating/ cooling rates of 3 °C/min, while during the nano-TA experiments the tip was heated extremely fast (600 °C/min). This difference might account for the ability of scanning probe thermal analysis to detect polymer re-organization phenomena on the sample surface which are not evident in larger volume samples heated at slower rates during the DSC experiments.

In addition to crystallization from the melt, PLA undergoes cold crystallization, upon heating from room temperature. For neat PLA samples used in this study, cold crystallization occurred above the glass transition temperature (59-61 °C) and below the melting transition temperature (179 °C) (Figure 6.11, and Table 6.4).

Figure 6.11 and Table 6.4 also show that the extent of cold crystallization depended on heating rate for both PLA L209S and PLA L210S. For both polymers, the temperatures of onset of cold crystallization ( $T_{icc}$ ), and the temperatures of the cold crystallization peaks ( $T_{cc}$ ) were higher for higher heating rates. The peaks were larger and sharper for the lower molecular weight polymer. Melting of PLA/xGnP-1 composites was also analyzed using DSC (Figure 6.12), and did not indicate cold crystallization processes.

Cold crystallization of PLA in the presence of xGnP-1 was exclusively detected by the nanoscale thermal analysis and is believed to be responsible for the *M*-shape of the deflection versus temperature curves obtained using scanning probe thermal analysis.



Figure 6.11 DSC thermograms showing the cold crystallization and melting of a) PLA L209S and b) PLA L210S at three heating rates



Figure 6.12 DSC thermograms showing the melting of a) PLA L209S/xGnP-1 and b) PLA L210S/xGnP-1 composites containing increasing amounts of xGnP-1

#### Conclusions

Scanning probe thermal analysis of two different molecular weight poly(Llactic acid) samples and their composites with exfoliated graphite nanoplatelets revealed essential differences in cold crystallization of the two polymer samples in the presence of the nanoplatelets as well as the dispersion of xGnP in the polymers. The difference in melting and crystallization behavior of the two polymers was not detectable by differential scanning calorimetry, which by itself could not explain the differences in the mechanical properties of the composites.

Nanoscale investigations of the thermal transitions occurring in polymer nanocomposites were proven to be important for the characterization of the dispersion of nanosize reinforcements, as well as for understanding the extent of their nucleating effect on semicrystalline matrices. The results show that xGnP is better dispersed in the higher molecular weight polylactic acid.

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# CHAPTER 7

#### CONCLUSIONS

Understanding how the crystallization of PHB and PLA is affected by addition of exfoliated graphite nanoplatelets is essential for designing multifunctional nanocomposites, since xGnP act as extremely efficient nucleating agents. The nucleation and growth of the crystalline structures formed in the presence of xGnP govern and also limit the properties of the nanocomposites. This research was directed at understanding the interactions of xGnP with PHB and PLA, with a goal that extended beyond filled systems, considering dimensional similarities between physical characteristics of polymers and the nanosize reinforcing particles, and exploring the polymer-particle interactions responsible for the improved properties of the polymer nanocomposites. The internal-out approach presented here offered quantitative information about the amount of xGnP required for nucleating purposes, and outlined the crystallization behavior of PHB/xGnP and PLA/xGnP composites incorporating higher amounts of graphite nanoplatelets in relation to other factors affecting the systems' behavior.

Amounts of xGnP-1 up to 1 % wt suffice for nucleating purposes, triggering a typical heterogeneous nucleating mechanism: in the presence of xGnP, crystallization from the melt is thermodynamically favored, maximum attainable

crystallinity is achieved faster and at higher temperatures. A kinetic study of the PHB/xGnP crystallization, employing a modified form of the Avrami equation, revealed that the presence of xGnP increased the PHB crystallization temperature, as well as the crystallization rates. Optical microscopy and atomic force microscopy investigations revealed the reduction in the size of PHB and PLA spherulites, indicating that the xGnP-nucleated polymers form smaller and more irregular crystalline structures and spherulitic morphologies specific for the neat polymers are no longer recognizable in the composites. X-ray diffraction showed that both PHB/xGnP and PLA/xGnP crystallize in the same crystal structure as the neat polymers.

Although microscopy techniques did not indicate significant differences between different composites containing amounts of xGnP higher than 3 % wt, for which properties were shown to depend on processing conditions, and on polymer molecular weight, differential scanning calorimetry revealed qualitative differences in crystallinity occurring in PLA/xGnP composites at higher xGnP loadings. DSC analyses successfully illustrated the competition between two effects of xGnP in polylactides matrices: nucleation, and retardation of crystal growth.

As part of this research, thermal analysis was further refined using scanning probe thermal analysis (nano-TA) as a novel characterization technique for investigating the morphology of these polymer nanocomposites. Nanoscale investigations of the thermal transitions in PLA/xGnP nanocomposites were important for the characterization of the dispersion of nanosized reinforcements,

as well as for understanding the extent of their nucleating effect on semicrystalline matrices. The information obtained using this technique complemented the conclusions derived from classical thermal analyses and offered additional insight on the relation between polymer confinement and molecular weight. The results are particularly important since they may be applied to nanocomposites utilizing similar semicrystalline polymer matrices.

Nanocomposite properties of the PLA/xGnP systems were investigated with a special focus on the relation between the nucleating effect of xGnP and change in mechanical properties and thermal conductivity. Although several processing methods were evaluated, the classical solvent mixing approach lead to highest improvement in all the properties evaluated. Using solvent mixing and compression molding, 30 % improvement PLA modulus was achieved with incorporation of as low as 0.01 % wt xGnP-1.

Regardless of the mixing and processing approach used, polymer confinement effects were observed in PLA/xGnP composites containing higher xGnP content. The addition of xGnP in excess of that required for nucleation resulted in the agglomeration of xGnP, and retardation of crystal growth.

Nanocomposites prepared both by melt mixing and solvent mixing showed that the same amount of xGnP was required for achieving electrical and the thermal conductivity. The nucleating effect of xGnP is a limiting factor in achieving high electrical and thermal conductivity in PLA/xGnP nanocomposites since the formation of large numbers of crystalline structures, thermodynamically favored by xGnP, isolates xGnP and prevents the direct contact of graphite

nanoplatelets in the resulted nanocomposites. The results suggest the possibility that not only the electron transport, but also the heat transport occurs through a percolation mechanism.

Thermal conductivity of PLA/xGnP nanocomposites can be improved by introducing a second phase to control the positioning of xGnP particles. Polystyrene, an amorphous polymer immiscible with PLA, was selected as a model polymer that when added to PLA and xGnP caused concentration of xGnP at the polymer-polymer interface creating a continuous xGnP path. Future work following this approach is suggested.

The findings are important for the design of nanocomposites from xGnP and PHB, and PLA, since the results outline the consequences of adding increasing amounts of graphite nanoplatelets to the polymers and approaches that can be used to target various properties.

On a larger scale, the study is of general interest for nanocomposites from similar semicrystalline polymer matrices in which nanoparticles act as nucleating agents.

#### Future work

The recent results regarding thermal and electrical conductivity imparted by xGnP to PLA matrices indicate that for achieving high conductivities in PLA and similar semicrystalline polymers, the focus needs to be on desirable changes in morphology that lead to lower percolation points.

Several ideas are suggested for achieving higher levels of thermal conductivity in PLA nanocomposites with xGnP. Taking advantage of polymer phase separation in binary blends is one possible approach that could prevent the encapsulation of xGnP in crystalline structures nucleated in the polymer matrix. The corresponding changes in mechanical properties are to be carefully monitored if following this approach. We also suggest the investigation of PLA/xGnP systems containing plasticizers, and the exploration of amorphous polylactides, and PLA mixtures containing D and L forms.

