Introduction
Dimensional similarities between physical characteristics of polymers (such as radius of gyration and lamellar thickness) and nano-sized reinforcing particles lead to the necessity to go beyond filled systems [1] and explore in detail polymer-particle interactions responsible for the improved properties of polymer nanocomposites. Dispersion is a key issue in processing polymer nanocomposites, and has a strong impact on mechanical properties. As opposed to phase separation (more likely to occur when incorporating micro-sized 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 nanocomposites [2].

In the case of semicrystalline polymer matrices, numerous nanoparticles used as reinforcements were shown [3-6] to act as heterogeneous nucleating agents and can be used as structure and morphology directors. Exfoliated graphite nanoplatelets (xGnP™ which is a trade mark of XG Sciences, Inc.) were shown to nucleate semicrystalline polymer matrices such as polypropylene [7], and poly(3-hydroxybutyrate) [8], determining dramatic changes in crystallization rates, polymer morphology, and properties of the resultant composites [9].

The present study focuses on using nano-TA for the evaluation of the nucleating effect of xGnP™ on a bio-polymer, poly(L-lactic acid), and on relating modifications in polymer’s morphology to changes in the mechanical properties of the composites.

nano-TA is a Localized Thermal Analysis technique which combines the high spatial resolution imaging capabilities of atomic force microscopy with the ability to obtain understanding of the thermal behaviour of materials with a spatial resolution of sub-100nm. The conventional AFM tip is replaced by a special nano-TA probe that has an embedded miniature heater and is controlled by the specially designed nano-TA hardware and software. The AFM enables a surface to be visualised at nanoscale resolution with its routine imaging modes, which allows
the user to select the spatial locations at which to investigate the thermal properties of the surface. The user then obtains this information by applying heat locally via the probe tip and measuring the thermomechanical response. There have been several examples in the literature of the application of sub-100nm LTA in the field of Polymers and Pharmaceuticals. [10-13].

**Experimental Details**

**Materials:** Two different molecular weight poly(L-lactic acid) samples were used in this study: RESOMER® L209S and RESOMER® L210S. Exfoliated graphite nanoplatelets having an average size of 1 μm (xGnP-1) was produced in-house [14, 15]. The xGnP has a surface area of ~100 m²/g and consists of platelets approximately 10 nm in thickness and 1 μm in diameter. Polyactic acid composites with expanded graphite nanoplatelets (PLA/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).

**Results and discussion**

**Crystallization of PLA/xGnP composites (DSC Analysis):** The storage moduli of PLA / xGnP-1 composites, increased with increasing amounts of xGnP-1 in the polymer matrix. 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.

As shown in Fig 1, 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, which indicated a nucleating effect of the nanoplatelets, similar to the nucleating effect observed recently in polyhydroxybutyrate/xGnP-1, and polypropylene/xGnP-1 composites [8,9]. For 1 % wt xGnP-1, a clear difference was observed in Fig 1 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 [16-18]. No significant differences in the melt crystallization behavior were observed between the composites of the two different molecular weight polylactides containing amounts of xGnP-1 higher than 1 % wt. 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 DSC analysis (Fig 2.) indicated that neat PLA L209S and PLA L210S melt at 179-180 °C. 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. As shown in Fig 2, the DSC analysis 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.

Fig. 2 DSC thermograms showing the cold crystallization and melting of (a) PLA L209S and (b) PLA L210S at three different heating rates

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. As shown in Fig 2, the DSC analysis 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.

Fig. 3 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
depending on the heating rate. **However, the DSC analysis did not detect cold crystallization after addition of xGnP-1 to either one of the polymer matrices.**

Figure 3 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 µm in diameter (Figure 3a). The addition of 0.01 % wt xGnP-1 lead to formation of much smaller crystalline structures (Figure 3,b), while crystalline structures were not detectable using optical microscopy when the amounts of xGnP-1 exceeded 1 wt %.

**Crystallization of PLA/xGnP Composites (nano-TA results)**

The melting behavior of PLA/xGnP-1 composites was further analyzed using nano-TA in order to investigate possible connections between agglomeration of xGnP and polymer molecular weight which were not evidenced by the DSC analysis. The results are shown in Fig 4 below. 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 \(T_{mo}\). nano-TA revealed three major differences in the melting behavior of the different molecular weight PLA and their composites with xGnP-1:

a) The recorded \(T_{mo}\) was lower (~ 150 °C) for PLA 209S than for PLA L210S (~159 °C). Lower temperatures were also recorded for the onset of melting transition of PLA L209S/xGnP-1 composites than for the PLA L210S/xGnP-1 counterparts.

b) The deflection curves for PLA L209S/ xGnP-1 composites were \(M\)-shaped, similar to the curves recorded for the neat polymer (Figure 4b). The deflection versus temperature curve for PLA L210S was also \(M\)-shaped (Figure 4a), but linear increases of deflection with temperature were recorded for the majority of the PLA L210S samples containing xGnP-1.

c) For all the PLA L209S/ xGnP-1 composites, the deflections recorded were lower than the
deflection measured for the neat PLA L209S (Figure 4b), while higher deflections were recorded for all PLA L210S/xGnP-1 composites than for the neat PLA L210S.

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 rearrangements that were not detectable by conventional thermal analysis (DSC). Third, the first peak could be a surface amorphous layer being formed. (This hypothesis will have to be studied as part of a separate study)

The possibility of different dispersion of xGnP-1 in the two molecular weight PLA samples was also indicated by Dynamic Mechanical Analysis (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. 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.

Nano-TA 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 nano-TA 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 2). Figure 2 also shows 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, and the temperatures of the cold crystallization peaks were higher for higher heating rates.
While further studies will need to be done to confirm this (as mentioned earlier), the authors believe that cold crystallization of PLA in the presence of xGnP-1 was exclusively detected by the nano-TA and is believed to be responsible for the $M$-shape of the deflection versus temperature curves. None of the other semicrystalline polymers that we used nano-TA on (at the same heating rates) - PHB, PE, PP, Nylon - showed such bimodal behaviour and PLA is the only one known to undergo cold crystallization

**CONCLUSIONS:** Exfoliated graphite nanoplatelets having an average diameter of 1 $\mu$m (xGnP-1) were shown to nucleate PLA, affecting both the cold crystallization and the crystallization from the melt of the polymer. They also had a reinforcing effect on PLA, leading to composites with improved mechanical properties and this reinforcing effect appeared to be dependent on the molecular weight of the polymer matrix. The same amount of xGnP-1 led to composites with higher modulus (up to 60 % improvement for 3 % wt xGnP-1) when incorporated into higher molecular weight PLA, and did not generate significant improvement in the case of a lower molecular weight matrix. Differences in the dispersion of xGnP-1 in the polymer matrices were suspected to be the essential cause for the differences in composites’ properties. Differential scanning calorimetry (DSC) revealed differences in the crystallization behavior depending on the molecular weight of PLA, but the results of this classical thermal analysis method could not be directly related to polymer’s morphology and to the dispersion of xGnP. Nano-TA measurements successfully detected differences in the crystallization behavior of PLA in the presence of xGnP, depending on the molecular weight of the polymer.

**REFERENCES**