Synergistic effects of filler size on thermal annealing-induced percolation in polylactic acid (PLA)/graphite nanoplatelet (GNP) nanocomposites

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Abstract Two graphene-based nano-fillers of different sizes were melt mixed with polylactide acid (PLA). Composite films based on graphite nanoplatelets (GNPs) with the largest lateral size showed superior electrical conductivity and a lower percolation threshold after melt-compounding and hot-pressing at room temperature. However, upon annealing in the melt, composites based on GNPs with the smallest lateral size displayed significantly improved electrical conductivity and a decrease in percolation threshold as a result of dynamic percolation while composites based on large GNPs showed hardly any change in conductivity and percolation threshold. Hybrid filler systems based on 5 wt% GNP with variable small/large GNP filler ratios displayed synergistic effects in the formation of a conductive network during thermal annealing, and an optimum filler ratio of 50/50 was found to achieve the highest conductivity after annealing. This annealing-induced increase in particle connectivity for composites based on 5 wt % hybrid small/large GNPs was also reflected in rheological measurements by the manifestation of a plateau in the storage modulus at low frequencies after annealing while such phenomenon was not observed for nanocomposites solely based on either small or large GNPs at similar loadings.

Keywords Graphene, Polylactide acid (PLA), Hybrids, Electrical properties, Conductivity, Dynamic percolation

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Introduction

Graphite nanoplatelets (GNPs), also called graphite nanosheets or nanoflakes, are a relatively new carbon nanomaterial composed of stacked 2D graphene sheets with outstanding mechanical and electrical properties.¹ Graphene-based nano-fillers have attracted particular interest as multifunctional fillers for improved mechanical, electrical, thermal, and barrier properties of polymer nanocomposites.¹⁻⁶

Over the years, several functional application fields like anti-static painting, EMI shielding,⁷ as well as sensing⁸⁻¹⁰ flexible electronics, and¹¹⁻¹³ field emission¹⁴ have been explored. Therefore, graphene or GNP is often hailed as the next generation nanofiller for multifunctional polymer systems.¹³

Melt compounding is a conventional way to produce nanocomposites on an industrial scale. However, often the electrical properties of such composites based on conductive nanoparticles like carbon nanotubes or graphene are disappointingly low,¹⁴⁻¹⁵ as shear mixing or compounding aims to disperse nanoparticles. In fact, well-dispersed nanocomposites are expected to exhibit maximum inter-particle distances and therefore a low degree of particle inter-connectivity and network formation and, as a result, low electrical conductivity. Network formation
of conductive nanoparticles in polymer composites is strongly affected by the processing history of these materials, and the optimization of processing methods that will maximize the electrical properties of conductive polymer composites (CPCs) is essential for a successful commercial implementation.

Annealing of polymer nanocomposites at temperatures above their glass transition temperature \( T_g \) is known to affect a variety of physical properties,\(^{19}\) most notably the electrical conductivities of composites based on conductive nanocarbons.\(^{20–26}\) Annealing has been shown to increase the electrical conductivity at room temperature (RT) of CPCs by several orders of magnitude.\(^{27}\) Systematic effects on electrical conductivity have been observed as a function of annealing temperature and annealing time and such relationship could be described using an Arrhenius equation related to polymer mobility.\(^{28,29}\) When a nanoparticle filled polymeric material is annealed at a temperature sufficiently above its \( T_g \) for a sufficient amount of time, the nanoparticles can reorganize themselves in the melt and their connectivity thereby increases as a result of a dynamic percolation process partly driven by van der Waals interactions. This increase in connectivity due to reagglomeration and network formation of nanoparticles under annealing manifests itself also in the rheological characteristics of a polymer melt, resulting in a more elastic behavior.\(^{30}\)

Such phenomenon as opposed to traditional statistical percolation is known as dynamic percolation. It means that, for the same concentration of nanofiller, a polymer composite can show very different conductivity levels as a result of different processing/thermal histories. Such phenomenon has been observed for one-dimensional (1D) carbon nanofillers like carbon nanotubes (CNT)\(^{24,27,30–32}\) and zero-dimensional (0D) carbon black\(^{25,33}\) filled polymer composites. Deng et al.\(^{24}\) reported a near five-time reduction in percolation threshold for oriented CNT/polypropylene (PP) tapes after annealing, while Zhang et al.\(^{27}\) found that the electrical conductivity of annealed films based on CNT/thermoplastic polyurethane (TPU) was up to eight orders of magnitude higher than that of as-extruded compound. Cipriano et al.\(^{28}\) studied multiwalled carbon nanotube (MWNT)/polystyrene (PS) and carbon nanofiber (CNF)/PS systems and observed an increase in conductivity with annealing time and temperature.

The effect of thermal annealing on the electrical properties of GNP/polymer composites and the influence of GNP size on network formation during annealing are however relatively unexplored. Li et al.\(^{34}\) examined the difference between diffusion displacement of small and large graphene-based fillers over a short time scale (2 min) in poly(methyl methacrylate) (PMMA) during multilayer coextrusion, but no further study on long-term annealing was reported. Kim et al.\(^{35}\) dispersed small functionalized graphene sheets and larger sized graphite in polycarbonate (PC)\(^{36}\) and poly(ethylene-2, 6-naphthalate) (PEN)\(^{37}\) matrix and reported improved conductivity for annealed samples. However, different sample geometries were used in this study thus an unequivocal conclusion on particle size effects in dynamic percolation could not be given.

Apart from annealing, the addition of a secondary conductive or even non-conductive filler on nanocarbon based CPCs was also reported to enhance the conductivity of these hybridized nanocomposites. Zhang et al.\(^{38}\) investigated the dynamic percolation in highly oriented conductive networks formed with different carbon nanofillers upon annealing and concluded that the addition of carbon black was able to accelerate the dynamic percolation process. Bilotti et al.\(^{39}\) reported controlled dynamic percolation in CNT/TPU composites by adding an insulating needle-like nanoclay (sepiolite) and found altered percolating networks of CNTs in TPU and a reduced percolation threshold. Despite significant interest in hybrid nanofiller systems, to the best of our knowledge, again no annealing studies have been reported for hybrid GNP-based systems.

Here we report on the influence of graphite nanoplatelet (GNP) size on electrical and rheological properties of PLA nanocomposites upon thermal annealing through the use of two types of xGNPs from XG Sciences, Inc. of different sizes. Small xGnP-C750 particles, large xGnP-M15 particles, and hybrids of both fillers were melt-compounded with polylactide acid (PLA) and resulting nanocomposite properties and behavior were evaluated before and after thermal annealing in the melt. Such multifunctional materials may be of interest for a variety of applications, most notably sensors.\(^{40}\)

## Experimental

### Materials

Poly(lactic acid) (PLA) (2002D – NatureWorks Co. Ltd., USA) with a density of 1.24 g/cm³, Young’s modulus of 3.5 GPa, strain at break of 6%, tensile strength of 60 MPa was purchased from Resinex (UK). GNPs were purchased from XG Sciences (Lansing MI, USA). xGnP-C750 and xGnP-M15 refer to graphite nanoplatelets with an average diameter of 1.2 and 14 μm, respectively, as measured in our lab and reported in our recent paper.\(^{41}\) According to the manufacturer, xGnP-C750 particles have a slightly lower thickness \( t = 2 \text{ nm} \) compared to xGnP-M15 \( t = 7 \text{ nm} \), which results in filler aspect ratios \( AR \) of ~600 for xGnP-C750 and ~2000 for xGnP-M15. Both GNPs are used as received.\(^{42}\) For simplicity and clarity, xGnP-C750 is referred to as GNP-S (small) and xGnP-M15 as GNP-L (large) in the context of this paper.

### Processing

Nanocomposites with 5, 7, 10, 13, and 15 wt% GNP in PLA were prepared by melt-compounding using an X’plore 15 cc mini-extruder (DSM, The Netherlands). Compounding was performed under nitrogen atmosphere at 180 °C. The screw speed was kept constant at 245 rpm for 9 min. Extruded strands were successively pelletized and compression molded at 180 °C and 50 bar for 3 min into disk-shaped samples with a thickness of 2 mm and a diameter of 25 mm. These disks were isothermally annealed in an oven (Thermo Scientific Heraeus®) at 200 °C under natural atmosphere for 0.5 and 1 h, respectively.

Nanocomposites with a total filler loading of 5 wt% but with varying GNP-S/GNP-L ratios \( (0.5/4.5, 1.5/3.5, 2.5/2.5, 3.5/1.5, 4.5/0.5) \) were processed using the same methodology as described above. Here, samples are denoted as PLA/GNP-S\(_x\)/GNP-L\(_{1-x}\), where \( x \) is the GNP-S loading in these hybrid filler-based nanocomposites.

### Characterization

The electrical conductivity of all hot-pressed samples was measured at room temperature (RT) by a two-point probe station using a Keithley 6485 picoammeter (Textronics, USA) and an Agilent 6614C DC voltage source (Hewlett Packard, USA).
Nanocomposites with a resistivity exceeding $10^{10}$ Ohm were considered as non-conductive as the electrical resistivity is here no longer measurable using the current experimental set-up.

Real-time dynamic percolation tests were conducted on the same rectangular samples as described above. Samples were heated on a hot plate from RT to a target temperature of 200 °C, with heating being discontinued after 2 h. Samples typically reached a temperature of around 180 °C, with conductivity, time, and sample temperature being monitored simultaneously, as described in our previous work on CNT-based dynamic percolation.17,18,28

Rheology was conducted on an AR 2000 Advanced Rheometer (TA Instruments, UK) connected to an environmental chamber with a 25-mm parallel plate setup. Hot-pressed disk-shaped samples were characterized at 180 °C using a frequency sweep ranging from 0.01 to 100 Hz and a strain of 0.1%, which is within the linear elastic region of the material.

Results and discussion

Electrical conductivity of nanocomposites

Figure 1 presents the electrical conductivity at RT for all nanocomposites before and after thermal annealing at 200 °C in an oven. Before annealing, both the addition of GNP-S and GNP-L nanofillers resulted in a significantly improved electrical conductivity of PLA at higher filler loadings. In the case of PLA/GNP-L nanocomposites, electrical conductivity increased already significantly for filler loadings of 7 wt%, while low aspect ratio GNP-S-based systems showed no electrical conductivity up to the relatively high filler loading of 10 wt%, indicating a much lower percolation threshold for GNP-L. Li et al.43 proposed an improved analytical model based on average inter-particle distances to predict the percolation threshold of polymer nanocomposites containing 3D randomly distributed disk-shaped nanoparticles. Assuming that particles are homogeneously distributed within the matrix and perfectly bonded to the polymer matrix, the critical volume fraction of 3D random distributed nanoplatelets can be expressed as:

$$V_{f,3D} = \frac{27\pi D^3 t}{4(D + D_{ip})^3} \quad (1)$$

where $D$, $t$, and $V$ are the diameter, thickness, and the volume fraction of the 2D particle, $D_{ip}$ is the inter-particle distance within which electron hopping occurs, resulting in a rapid increase in electrical conductivity of the composite. Therefore, the $D_{ip}$ parameter in Equation (1) is not a mathematical constant, but represents the influence of properties of the polymer matrix material on the electrical behavior of the composite. It is reported that according to quantum-mechanical tunnelling mechanisms,44 electron hopping can take place between adjacent conductive fillers when $D_{ip} \leq 10$ nm. This phenomenon was reported to be independent of the resistivity of the polymer matrix and is applicable to most polymers, organics, and oxides. Thus, a $D_{ip}$ of 10 nm is adopted in this study.

Note that the diameters of both small and large GNP (1.2 and 14 μm) are two to three orders of magnitude higher than the required $D_{ip}$ (10 nm), meaning that the influence of $D_{ip}$ can be neglected and the equation can be further simplified as:

$$V_{f,3D} = \frac{27\pi D t}{4D^3} = \frac{27\pi}{4AR} \quad (2)$$

The extruded strands were successively pelletized and compression molded at 180 °C and 50 bar for 3 min into disk shapes (diameter; 25 mm, thickness; 2 mm) using a Collin P300E hot press (Dr. Collin, Germany). From these disks, samples with dimensions 20 mm × 5 mm × 2 mm were cut and silver paste coating was used to ensure good contact with the electrodes of the electrometer. Annealed samples were taken from the oven and left to cool to RT before testing. Specimens with a resistivity exceeding $10^{10}$ Ohm were considered as measurable data are plotted as $10^{-10}$ S/m and is represented by the shaded gray area.
area represents the non-measurable conductivity range

GNP-S flakes have greater mobility in the PLA melt, leading to unchanged percolation threshold. This suggests that smaller rigid network that hinders motion of individual nanofillers, network. On the contrary, high filler loadings result in an initial conductive networks even after prolonged annealing times different for both systems.

These unaltered electrical properties with annealing are very different for nanocomposites containing 3.5 and 4.5 wt.% GNP-S, while composites became non-conductive again when the entire filler content (5 wt%) was made up of GNP-S. Such change from insulator to conductor to again insulator with increasing GNP-S content is indicative of significant synergistic effects between small and large nanofillers and suggests that small GNP-S is mainly responsible for creating the conductive network through dynamic percolation while a minimum GNP-L content is required for the initial filler framework through which a conductive network can form after annealing. Meaning that, while a critical amount of GNP-S is needed for dynamic percolation, a small amount of GNP-L is still required to reduce the inter-particle distances further to effectively form a conductive network. This also explains why the system based solely on 5 wt.% GNP-S remains non-conductive even after 1 h annealing.

**Figure 3** Real-time electrical conductivity measurements, showing the time dependence of the electrical properties of PLA/GNP nanocomposites when subjected to a temperature scan

Notes: Nanocomposites based on hybrid small- and large GNP-S showed a secondary increase in electrical conductivity around the polymer melting temperature, indicating dynamic network formation and electrical properties which are mostly maintained after cooling to RT. Red: PLA/GNP-S5, Blue: PLA/GNP-L5, Green: PLA/GNP-S2.5/GNP-L2.5, Black: Temperature scan. Shaded gray area represents the non-measurable conductivity range

where $AR$ is the aspect ratio of the nanoplatelet ($AR = D/t$). From this, it can be concluded that larger aspect ratio conductive fillers give lower percolation thresholds, which is in agreement with our experimental data with the larger GNP-L based systems exhibiting a lower percolation threshold than systems based on GNP-S after compounding.

Interestingly, the effects of particle size on electrical conductivity after annealing are very different. Upon annealing, GNP-S-based nanocomposites showed a significant increase in conductivity for systems with medium GNP-S loadings (7 to 10 wt%), while the percolation threshold shifts from around 13 wt% GNP-S to values of around 7 wt%. Both 5- and 15 wt% -based systems remain unchanged as non-conductive and highly conductive, respectively. In contrast, the PLA/GNP-L system showed hardly any change in conductivity for all concentrations upon annealing, resulting in an unchanged percolation threshold. This suggests that smaller GNP-S flakes have greater mobility in the PLA melt, leading to increased migration and network formation by reaggregation during annealing than larger GNP-L flakes. It should be noted that it is not necessarily the nanoparticle that moves but the polymer molecules that diffuse/relax around the nanoparticle, only indirectly causing “motion” or reorganization of the nanoparticle’s (relative) position, a reduction of inter-particle distance and an increase in electrical conductivity.

Although electrical properties remain unaffected for both the 5- and 15 wt% -based composites, the reasons behind these unaltered electrical properties with annealing are very different for both systems.

Composites with too low filler loadings are not able to form conductive networks even after prolonged annealing times as a minimum amount of filler is required to create such a network. On the contrary, high filler loadings result in an initial rigid network that hinders motion of individual nanofillers, leading to a network which is unaffected by annealing. This explains why 15 wt% PLA/GNP-S systems showed little change in conductivity upon annealing. Similarly, only a small increase in electrical conductivity was observed for 13 wt% PLA/GNP-S after 0.5 h annealing. In short, whenever an initial network is present, the system becomes rigid and demonstrates less nanoparticle migration, meaning a limited effect of annealing on electrical properties.

To further investigate the importance of filler size on dynamic percolation, hybrid filler systems based on a fixed total amount of GNP-S (5 wt%) but with a variable GNP-S/GNP-L ratio were melt compounded, and the conductivity after annealing was measured and plotted in Figure 2.

Hybrid nanocomposites with 0, 0.5, and 1.5 wt% of GNP-S were non-conductive even after 1 h of annealing. However, when the content of GNP-S reached 2.5 wt%, i.e. a 50/50 hybrid filler ratio (GNP-S2.5/GNP-L2.5), conductivity increased dramatically by five orders of magnitude after 0.5 h of annealing and increased further by nearly two orders of magnitude after another 0.5 h annealing. Smaller increments were observed for nanocomposites containing 3.5 and 4.5 wt% GNP-S, while composites became non-conductive again when the entire filler content (5 wt%) was made up of GNP-S. Such change from insulator to conductor to again insulator with increasing GNP-S content is indicative of significant synergistic effects between small and large nanofillers and suggests that small GNP-S is mainly responsible for creating the conductive network through dynamic percolation while a minimum GNP-L content is required for the initial filler framework through which a conductive network can form after annealing. Meaning that, while a critical amount of GNP-S is needed for dynamic percolation, a small amount of GNP-L is still required to reduce the inter-particle distances further to effectively form a conductive network. This also explains why the system based solely on 5 wt% GNP-S remains non-conductive even after 1 h annealing.

**Real-time monitoring of conductivity**

To further investigate the dynamic percolation behavior of PLA/GNP composites based on either 5 wt% GNP-S, 5 wt% GNP-L, and 5 wt% 50/50 hybrids (consisting of 2.5 wt% GNP-S and 2.5 wt% GNP-L), real-time measurements of conductivity were conducted on selected samples and results are presented in Figure 3. All three PLA nanocomposite samples start to show an increase in conductivity at around the glass transition temperature of PLA ($T_g = 76 \degree C$), and follow the same temperature-dependent electrical conductivity trend until a temperature of around 140 °C (i.e. close to $T_{m} = 167 \degree C$). However, above this temperature, the GNP-S2.5/GNP-L2.5 hybrid nanofiller system showed a strong additional increase in conductivity, reaching a high constant conductivity value in the melt at a temperature of around 180 °C. The overall conductivity of the PLA/GNP composites, $\sigma(f)$, can therefore be expressed as

$$\sigma(f) = \sigma(T) + \sigma(reaggr)$$

where $\sigma(T)$ is the temperature-dependent conductivity of the composites and $\sigma(reaggr)$ is the reaggregation-induced network-controlled conductivity of the composites.

The two distinct stages in the temperature dependence of the electrical conductivity of the hybrid nanofiller-based composite suggest that in this system a secondary conduction
did also not show a secondary increase in conductivity above $T_m$ but here the absence of dynamic percolating is due to the low aspect ratio of GNP-S, preventing this system from forming such a network.

In the first heating stage from RT to around 140 °C (below $T_m = 167$ °C), the temperature-induced conductivity is dominant for all three composites as the polymer is still in the solid state and no major reorganization of GNPs in the polymer matrix can occur. This explains the initial increase in conductivity with time during heating as seen in Figure 3. However, after reaching the PLA melting temperature, especially the small nanoparticles start to migrate and rearrange themselves, creating new conductive pathways. During annealing, small GNPs will gain mobility through heating and may reconnect to minimize the overall surface free energy.

After heating is removed, conductivity of all three nanocomposites decreases instantaneously. Interestingly, both the PLA/GNP-S$_5$ and PLA/GNP-L$_5$ systems lose nearly all there conductivity after cooling to RT, while the hybrid PLA/GNP-S$_2.5$/GNP-L$_2.5$ system maintains a high level of conductivity even after cooling. These differences are a strong indication that mechanism is active, which results in a strong increase in conductivity of this nanocomposite system. During heating from RT to just below $T_m$, the measured electrical conductivity is solely dependent on the temperature dependence of the electrical conductivity$^{45-47}$ for all three nanocomposite systems. However, close to or above the PLA melting temperature, the GNP-S in the hybrid system gains mobility and reorganizes itself into a reaggregated network. The driving forces for such a reorganization mechanism are thermodynamic processes that minimize surface free energy. For a given volume of GNPs in the matrix, well-dispersed GNPs will have a much higher surface-to-volume ratio compared to GNP aggregations. This phenomenon results in an additional contribution of the reaggregated network to the overall electrical conductivity and is observed through a change in slope of the conductivity versus time curve for the PLA/GNP-S$_2.5$/GNP-L$_2.5$ hybrid composites as shown in Figure 3.

On the other hand, nanoparticle migration is less obvious for GNP-L as these nanoparticles exhibit less mobility and as a result conductivity changes little for PLA/GNP-L$_5$ for the same annealing time. Similarly, composites based solely on GNP-S$_5$ did also not show a secondary increase in conductivity above $T_m$ but here the absence of dynamic percolating is due to the low aspect ratio of GNP-S, preventing this system from forming such a network.

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Figure 4 SEM images of PLA/GNP-S (top) and PLA/GNP-S/GNP-L (bottom) composites along the measured electrical conductivity direction before (left) and after (right) annealing.
the increase in conductivity for the hybrid nanofiller system during heating is the result of a reorganization of the nanofiller network, which remains present after cooling to RT and results in high sustained electrical properties. Nanocomposites solely based on either small- or large GNP nanofillers did not show this dynamic network formation and temperature-dependent conductivity is lost upon cooling to RT. Please note that heating conditions for PLA/GNP-S in Figure 2 are different from those in Figure 3 so the data are not directly comparable.

**Morphology of nanocomposites before and after annealing**

To further investigate potential mechanisms responsible for the increase in conductivity with annealing, SEM images were taken of composites before and after annealing as in Figure 4. For PLA/GNP-S, little information was revealed regarding changes in distances between GNPs, possibly due to the small size of GNP-S which made them very difficult to observe under SEM. For PLA/GNP-S/GNP-L, the distance between the GNP-L hardly changed after annealing, which is consistent with our hypothesis that increased filler connectivity in the hybrid system is mainly attributed to the migration of GNP-S.

**Rheology of nanofiller networks**

It is believed that the recovery of conductivity in GNP-based nanocomposites after annealing is due to the re-establishment of connections between nanoparticles that were initially lost during shear mixing. Dynamic rheology of samples before and after annealing is a powerful tool to establish a link between electrical conductivity and composite morphology. Measurement of the in-phase shear modulus $G'$ as a function of frequency is a sensitive tool to characterize the formation of a network by nanoparticles in a polymer melt. The presence of such a network manifests itself as a plateau in the in-phase $G'$ shear modulus at low frequencies, of which the magnitude of this $G'$ plateau is known to correlate with a number of connections in the network (i.e. the network density).

Figure 5 shows frequency sweeps at 180 °C for selected PLA/GNP samples before and after annealing for different periods of time. The results are particularly notable for the PLA/GNP-S$_{2.5}$/GNP-L$_{2.5}$ hybrid samples. For these systems, $G'$ levels off significantly at low frequency finally reaching a plateau value at low frequencies after 1 h annealing, suggesting typical solid-like behavior of the nanocomposite melt as a result of the established network of filler–filler contacts. This indicates that a conductive network was formed for this nanocomposite system after 1 h of annealing. This further supports our hypothesis that GNP-L acts as the backbone of the network, while GNP-S acts as migrating branches filling the inter-particle voids, leading to a higher network density.

PLA/GNP-S$_{5}$ and PLA/GNP-L$_{5}$, on the other hand, did not show a low-frequency plateau in its $G'$. In fact, $G'$ hardly changed after 0.5 and 1 h annealing for both systems. This is in agreement with our previous discussion and indicates that the network connectivity in these formulations remains unchanged and explains why annealing did not alter the conductivity of these systems.

Figure 5 suggest a stronger rheological filler network when GNP of different sizes are used particularly after annealing. However, this is not necessarily the consequence of improved dispersion as optimal dispersion implies maximum inter-particle distances and would be evidenced by a decrease in electrical properties, which is opposite to what is shown in Figure 1.

**Nanofiller mobility and influence of filler size**

It is worth considering how or why annealing can re-organize nanoparticles into an interconnected state. Randomization of nano-scale hard disks can be governed by either Brownian motions of particles, or non-Brownian interactions.

First, we will consider Brownian motion of particles. Rotational diffusivity $D_r$ of a circular Brownian disk with a diameter $d$ in a medium with a viscosity $\eta$ at temperature $T$ can be expressed as

$$D_r = \frac{3kT}{4\eta d^2}$$

(4)

Given the same temperature, at dilute or semi-dilute concentrations, the ratio of displacement between small and large GNPs can be derived as

$$\frac{D_{S}}{D_{L}} \sim \frac{d_{L}^2}{d_{S}^2}$$

(5)

Based on this consideration, small GNP-S ($d = 1.2 \mu \text{m}$) are expected to display nearly 1600 times larger displacements than large GNP-L ($d = 14 \mu \text{m}$) under the same conditions. Such a huge difference in GNP mobility explains why annealing is much more effective for small GNPs than for large GNPs.

Next, we may also consider non-Brownian interactions. Apart from limited translational and rotational diffusion dominated by Brownian motions, particles may still be able to reorient, even under non-Brownian conditions due to the
It should be noted that our data (see Figures 1 and 2) indicate that only systems with semi-dilute GNP-S filler concentrations show dynamic percolation and filler network formation after annealing. Similar differences caused by filler concentration were also observed by Kim et al.\textsuperscript{36} and are schematically depicted in Figure 6. At very dilute concentrations, even complete randomization of GNP-S will not result in particle–particle contacts since their spheres of rotation do not intersect as indicated in Figure 6(a). This explains the unchanged conductivity for composites incorporating 5 wt% GNP-S as shown in Figure 1, i.e. the number of particles is not high enough to create a percolating network. PLA composites incorporating small GNP-S fillers are more affected by annealing as a lower activation energy is required for dynamic percolation in this system. Further experiments to quantify this effect will be designed in the future to validate such a hypothesis.

The viscoelastic nature of the polymer matrix following Arrhenius behavior:\textsuperscript{55}

\[
\eta = c \exp \left( \frac{\Delta E}{RT} \right) \tag{6}
\]

where \(T\) is temperature, \(R\) is the ideal gas constant, \(\Delta E\) is an activation energy, and \(c\) is a constant. \(\Delta E\) implies the fillers resistance to reorientation and can be obtained by fitting the data at different temperatures using Equation (6). It has been reported that longer carbon nanotubes tend to have a higher \(\Delta E\) thus requiring more energy to reorient.\textsuperscript{35} In other words, they need higher annealing temperatures and/or longer annealing times. This also explains why PLA composites incorporating small GNP-S fillers are more affected by annealing as a lower activation energy is required for dynamic percolation in this system.

Figure 6 Reorientation mechanisms during annealing for GNP-S in: (a) dilute (5 wt%), (b) semi-dilute (7–10 wt%) and (c) concentrated regime (15 wt%)

Note: Increased connectivity through annealing can only be achieved within the semi-dilute regime.
which gives rise to the increased in-plane shear modulus $G'$ and electrical conductivity for PLA/GNP-S composites with intermediate filler loadings (7 and 10 wt% GNP-S). However, in the concentrated regime (Figure 6c), isotropic (re)orientation cannot take place due to excluded volume interactions between particles, hence leading to limited changes in conductivity upon annealing. This is illustrated by the fact that electrical conductivity of composites based on 15 wt% GNP-S remains unchanged even after 1 h of annealing.

Conclusions

In this study, we have shown that smaller GNP nanoparticles exhibit a much greater ability to form a conductive filler network by dynamic percolation during thermal annealing than larger nanoparticles.

This network forming ability of small GNP in a polymer melt could be particularly exploited when hybridized with large GNP, leading to significant synergistic effects in electrical properties of resulting PLA nanocomposites. Electrical conductivity of hybrid nanocomposites incorporating both small GNP-S and large GNP-L nanofillers was greatly improved by thermal annealing at elevated temperatures, while those of composites solely based on similar amounts of GNP-S and GNP-L remained largely unchanged under the same annealing conditions.

Similarly, rheological properties specifically the in-plane shear modulus $G'$ at low frequencies increased with annealing for nanocomposites incorporating hybrid nanofillers suggesting network formation. The microstructural basis for these observations is that initially filler–filler contacts are lost due to the high shear forces during compounding and that these can be re-established, albeit through a different network morphology, during thermal annealing in the melt, leading to greatly improved electrical properties as a result of dynamic percolation.

The results presented in this study have significant practical relevance for the large-scale manufacture of conductive polymer nanocomposites as it provides guidelines of how to achieve good electrical properties at low filler loadings.

Disclosure statement

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