1. INTRODUCTION

Industries have been shifting into sustainable alternatives, and the use of biodegradable/biocompatible materials has been the focus of various groups. Poly(ethylene oxide) (PEO) is a biocompatible, semicrystalline polymer used in various applications; solid electrolytes, for drug delivery, in biomedical scaffolds, and for polymer fabrication. An easy way to create robustly advanced materials from such a polymer is through nanoparticle (NP) incorporation. Since PEO is a semicrystalline polymer with a high degree of crystallinity, the corresponding nanocomposite and blend properties are highly affected by changes in the crystallization kinetics and the final semicrystalline PEO morphology. Thus, many studies have focused on understanding how NP addition affects crystallization kinetics — this topic is precisely the focus of this paper.

Incorporating lignin as a filler is a direct path toward developing economically and sustainably appealing polymer nanocomposites. Lignin is a renewable and naturally available material, considered the second most abundant biomacromolecule (after cellulose). Lignin is also relatively inexpensive, biodegradable, and has substantial antioxidant and antibacterial properties. Therefore, the preparation of polymer hybrid materials, with lignin as a filler, has been the scope of several studies. It was shown that polymer/filler compatibility plays a major role in enhancing the crystallization kinetics of the hybrid, where incompatible, phase-separated mixtures always lead to undesired results and deteriorated properties. Although lignin shows unfavorable interactions with most synthetic polymers and natural rubbers, it has good affinity to PEO. Kubo and Kadla have shown that lignin forms strong hydrogen bonds with PEO chains, usually leading to compatible mixtures over a wide range of PEO molecular weights. They have also shown that PEO/lignin mixtures exhibit a single glass-transition temperature that increases as the lignin content increases. Such behavior, which presumably resulted from well-dispersed highly interacting lignin NPs, has been confirmed by Wu et al. and others.

This paper compares the nucleation efficiency of LNPs against that achieved by inorganic NPs (e.g., silica); we also examine their effect on decreasing spherulitic growth kinetics. Previous works have shown that inorganic NPs act as nucleating or antinucleating agents based on their dispersion states, surface chemistry, aspect ratio, and loadings. That is, well-dispersed and surface-modified NPs can act as...
heterogeneous nucleation sites that lead to orders of magnitude increase in nucleation efficiency, as confirmed by various studies. 30,33 As aggregation usually occurs upon increasing NP concentration, the nucleation efficiency tends to decrease, resulting in an optimum at moderate loadings. 34 In terms of growth kinetics, the incorporation of spherical NPs usually decreases the spherulite growth rate beyond a specific concentration. 35 The extent of such decrease is mainly affected by NP content (interparticle spacing), surface chemistry, and NP aggregation. 36 Altobraq et al. 36,37 have shown that grafted NPs lead to a relatively larger decrease in the spherulitic growth rate compared to observations with bare NPs.

Here, we characterize the LNP dispersion state and its affinity with the PEO matrix through scanning electron microscopy (SEM) and Fourier transform infrared (FTIR), respectively. We then study the effect of LNP content, dispersion state, and surface chemistry on the nucleation and growth kinetics of PEO using polarized light optical microscopy (PLOM). Finally, we evaluate the overall crystallization kinetics in both isothermal and nonisothermal protocols using differential scanning calorimetry (DSC) and enunciate how the nucleation and growth steps separately contribute to the observed overall crystallization kinetics.

2. EXPERIMENTAL SECTION

2.1. Materials. PEO (viscosity average molecular weight, Mv = 100 kDa) was purchased from Sigma-Aldrich (Madrid, Spain). Lignin from spruce and ionic isolation process was used. The isolation method is a patented procedure (DE102010048614A1) that uses imines. The main characteristics of lignin are: ash content = 0.6 wt %, moisture content = 23.34 wt %; C, N, S, H contents = 66.26, 0.26, 0.71, and 8.27%, respectively; molecular weights Mw and Mz = 3718 and 768 Da, respectively. 37 Sodium dodecyl sulfate (SDS, Andeira) and tetrahydrofuran (THF, Cicarelli) were used as received.

2.2. Synthesis of Lignin Nanoparticles. LNPs were prepared using an ultrasonication method, as illustrated in Figure 1. Lignin was first dissolved in THF at a concentration of 0.3% w/v. The solution (15 mL) was then added dropwise into a reactor containing 50 mL of using an ultrasonication method, as illustrated in Figure 1. Lignin was and tetrahydrofuran (THF, Cicarelli) were used as received.

2.3. Sample Preparation. Solution mixtures of PEO (5 wt %) and LNPs (1 wt %) in water were first prepared. Different PEO/LNPs weight compositions were mixed: 95/05, 90/10, 85/15, and 80/20. These mixtures were stirred for one hour at room temperature, and then solvent-cast onto silicon molds. The resulting films were dried at room temperature and then under high vacuum at 50 °C for 1 day.

2.4. Dynamic Light Scattering. Dynamic Light Scattering (DLS) was performed using Malvern Instruments (Zetasizer Nano Z) to determine the mean LNP size. The light source is a He–Ne laser with a wavelength and a scattering angle of 633 nm and 173°, respectively. The suspensions were prepared by dispersing the solid powder in ultrapure water at a concentration of about 0.1 g/L, then treated for 6 min in an ultrasonic bath. The measurements were performed at room temperature.

2.5. Fourier Transform Infrared Spectroscopy. FTIR measurements of neat LNP, neat PEO, and PEO/LNP nanocomposites were conducted on a Shimadzu Model 8201 Fourier transform spectrophotometer in the frequency region of 4000–500 cm−1 at 40 scans. Potassium bromide (KBr) disks were employed to avoid interferences in the absorbance and obtain higher resolution spectra. The resulting spectra were then processed using Hyper IRR software.

2.6. Scanning Electron Microscopy. Scanning electron microscopy (SEM) was performed using Nova NanoSEM 450 (FEI) instrumentation at Columbia University’s Clean Room Laboratory. The instrument is equipped with a FEG electron gun that uses an ultra-high brightness Schottky field emitter. The secondary electron mode was used for imaging at an acceleration voltage of 5 kV. The samples were first cryo-fractured, then mounted on a stub using copper tape, and then sputter-coated with Ag/Pd using a Cressington 108 manual sputter coater instrument for one minute to reduce charging (6 nm thick layer).

2.7. Differential Scanning Calorimetry. Calorimetry experiments were performed using a PerkinElmer DSC 8000 instrument equipped with an Intracooler II. The DSC was calibrated with indium and tin standards. Samples of ~5 mg mass were encapsulated in aluminum pans and sealed. Ultra-high purity nitrogen was used to provide an inert atmosphere. For the nonisothermal analysis, the heating and cooling rates were 20 °C/min. The samples were first heated from 25 to 100 °C, kept for 3 min at 100 °C to erase thermal history, and then cooled to −70 °C; the corresponding cooling scans were recorded. The samples were then heated to register the subsequent heating scans.

For the isothermal crystallization studies, the experiments were carried out following the detailed procedure recommended by Müller et al. 50 Samples were heated to 100 °C at 20 °C/min and kept at that temperature for 3 min to erase any previous history. Then, the samples were cooled at 60 °C/min to the chosen isothermal crystallization temperature (Tc). The Tc range employed for each sample was previously determined by preliminary tests to ensure that no crystallization occurred during the cooling step.

Self-nucleation (SN) measurements were performed according to the Fillon et al. experimental protocol. 39,41 The samples were heated to 120 °C for 3 min to erase thermal history. Then, a standard thermal history was created by cooling the samples at 20 °C/min to
20. Scale bars are 1 μm. LNPs appear brighter due to their higher electron density compared to the PEO matrix.

Figure 2. Scanning electron microscopy (SEM) images of the PEO/LNP nanocomposites. PEO/LNP weight ratios are (a) 95/05 and (b–d) 80/20. Scale bars are 1 μm. LNPs appear brighter due to their higher electron density compared to the PEO matrix.

Figure 2a,b shows the LNP dispersion states as characterized by SEM at loadings of 5 and 20 wt %, respectively. Regardless of loading, the LNPs are well dispersed in the PEO matrix, except for some slight aggregation observed in certain areas of the sample with 20 wt % LNPs (see Figure 2d). Figure 2b–d shows LNP dispersion states in different regions of the same sample with the highest loading. The good dispersion is likely due to the favorable hydrogen bond interaction between the PEO and LNP. This is in good agreement with the works of Wu et al.,19 and Kubo and Kadla,26 who have shown that the PEO and lignin are compatible and hence well dispersed over the entire compositional range. FTIR evidence for hydrogen bonding between the nanocomposite’s components is provided below.

3. RESULTS AND DISCUSSION

3.1. LNP Dispersion and Compatibility. The LNP size and its distribution are discussed in the Supporting Information (DLS measurements and TEM and AFM images of LNPs). Figure S1 shows that the size distribution of LNPs is broad; such a high dispersity is intrinsic to the sonication method employed here. For more details on the LNP synthesis, the reader is referred to the published works,37,43 here, we focus mainly on the LNP/PEO dispersion state and crystallization kinetics.

Figure 2a,b shows the LNP dispersion states as characterized by SEM at loadings of 5 and 20 wt %, respectively. Regardless of loading, the LNPs are well dispersed in the PEO matrix, except for some slight aggregation observed in certain areas of the sample with 20 wt % LNPs (see Figure 2d). Figure 2b–d shows LNP dispersion states in different regions of the same sample with the highest loading. The good dispersion is likely due to the favorable hydrogen bond interaction between the PEO and LNP. This is in good agreement with the works of Wu et al.,19 and Kubo and Kadla,26 who have shown that the PEO and lignin are compatible and hence well dispersed over the entire compositional range. FTIR evidence for hydrogen bonding between the nanocomposite’s components is provided below.

Figure 3a shows FTIR spectra separately for the neat PEO and LNP. For the pristine LNPs (dashed-curve), characteristic bands observed in the range of 600–3900 cm\(^{-1}\) correspond to OH stretching—3700–3100 cm\(^{-1}\) (L1), alkyl stretching—2921 cm\(^{-1}\) (L2), aromatic C=C stretching—1519 cm\(^{-1}\) (L3), phenolic –OH bending—1463 cm\(^{-1}\) (L4), aromatic skeleton—1600 cm\(^{-1}\) (L5), C–O–C stretching—1224 (L6) and 1083 (L7) cm\(^{-1}\). In the case of neat PEO (solid curve), the characteristic bands correspond to aliphatic –CH stretching—2879 cm\(^{-1}\) (P1), –CH bending—1467 cm\(^{-1}\) (P2), C–O–C (symmetric and asymmetric) stretching- 1096 cm\(^{-1}\) (P3), and CH\(_2\) rocking vibration—836 cm\(^{-1}\) (P4). Note that the –OH band from lignin is more intense than the corresponding band from the PEO due to the multiple OH groups in the lignin structure.

The FTIR spectra of polymer nanocomposites (with LNP contents of 10, 15, and 20 wt %), shown in Figure 3b, are compared to the neat PEO and the pristine LNP to confirm the molecular interactions between the mixture components. Upon the incorporation of LNPs into the PEO matrix, the characteristic broadband of OH groups in the LNP is slightly shifted to lower wavenumbers. Additionally, the intensity of the aromatic skeleton characteristic band at 1600 cm\(^{-1}\) (LP2) of the composites increases with LNP contents (i.e., 10 vs 20 wt %). Previous work attributed the shift of the characteristic band of –OH groups to the formation of intermolecular hydrogen bonds, and it is in good agreement with our results. In addition, the –OH band was deconvoluted into two peaks corresponding to hydrogen-bonded –OH and free OH, and the results are presented in the Supporting information (Figure S2).

3.2. Effect of LNP on PEO Nucleation Kinetics. PLOM is employed to measure the nucleation density (\(\rho_{\text{nuclei}}\)) of PEO/LNP nanocomposites according to the experimental procedure discussed in Section 2.8. Figure 4 plots \(\rho_{\text{nuclei}}\) vs time.
To get a direct measure of the primary nucleation kinetics, we evaluate the nucleation rate \( I \) of the nanocomposites (Figure 5) by taking the time-derivative of \( \rho_{\text{nucle}} \) at short times where the dependence is linear \( I = \partial \rho_{\text{nucle}} / \partial t \). The Turnbull–Fisher (TF) model \(^{44-46} \) is used to describe the experimental data in Figure 5

\[
\log I = \log I_0 - \frac{\Delta F^\#}{2.3kT} - \frac{16\sigma_0(\Delta \sigma)T_m^{0.2}}{2.3kT(\Delta T)^2(\Delta H_m)^2}
\]  

(1)

where \( I_0 \) represents contributions from the diffusion of polymer segments to the nucleation site, \( k \) is the Boltzmann constant, \( \Delta F^\# \) is a parameter related to the primary nucleation free energy, \( \sigma_0 \) and \( \sigma \) are, respectively, the fold and lateral surface free energies, \( \Delta H_m \) is the volumetric melting enthalpy \( \Delta H_m = \Delta H_m(\rho) \), \( \Delta F_m^\# \) is the melting enthalpy of 100% crystalline PEO (214 J/g), \( \rho \) is the PEO density (1.13 g/cm\(^3\), reported by the manufacturer). \( \Delta T \) is the undercooling (i.e., \( \Delta T = T_m^\# - T_c \)), where \( T_m^\# \) is the equilibrium melting temperature \( (T_m^\# = 79 \, ^\circ \text{C}) \). \(^{48} \) The detailed procedure of parameter evaluation is presented in the Supporting Information (see Table S2). The melt-nucleus interfacial free energy difference \( (\Delta \sigma) \) is then determined from the TF fit in Figure 5 (i.e., \( \Delta \sigma \) is proportional to the slope).

Figure 6 plots \( \Delta \sigma \), a measure of the free energy difference between the heterogeneous nucleus and the melt, as a function of LNP content. Clearly, the incorporation of LNP leads to an unexpected decrease in \( \Delta \sigma \) as a function of LNP content, with the results effectively flattening out to within uncertainties at larger NP loadings. Thus, a lower free energy difference caused by the incorporation of LNP suggests more stable nucleus formation, leading to higher nucleation density even at temperatures elevated compared to neat PEO. Such a decrease in \( \Delta \sigma \) has been linked to higher nucleation efficiencies. \(^{34,44,49} \)

Furthermore, the saturation of the nucleation at 15% could be an indication that NP aggregation sets in; the “larger” NPs observed in Figure 2d at 20% loading are consistent with this interpretation. The trend reported in Figure 6 is also consistent with the nucleation efficiency of the LNP, as we will discuss below (see Figure 11 and its discussion).

3.3. Effect of LNP on PEO Growth Kinetics. PLOM measurements are conducted to delineate the effect of LNP on the PEO spherulitic growth rate \( (G) \). Figure 7a,b summarizes changes in \( G \) and relative growth rate \( (G/G_{\text{PEO}}) \), respectively, for the different LNP content as a function of isothermal crystallization temperature. Figure 7a shows that LNP reduce the experimentally determined spherulitic growth rates when crystallizing at similar \( T_c \). Such a decrease in the growth kinetics is presumably due to the PEO/LNP interactions which affect the diffusion of the chains to the growth front.

The Lauritsen–Hoffman (LH) model \(^{50,51} \) is used to fit the spherulitic growth rates (solid lines in Figure 7a)

\[
G = G_0 \exp \left( \frac{-U^*}{R(T - T_\infty)} \right) \exp \left( \frac{-K_0^2}{kT \Delta T} \right)
\]  

(2)

where \( G_0 \) is a preexponential growth rate constant, \( U^* \) is the transport activation energy of the polymer chain (commonly taken as 1500 cal/mol [6280 J/mol]), \( K_0^2 \) is a parameter proportional to the secondary nucleation activation energy, \( R \) is the universal gas constant \( (8.134 \, \text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}) \), \( T_\infty \) is the temperature at which chain dynamics ceases \( (= T_g - 30) \), and \( f \)
is a temperature correction factor \( f = 2T_c/(T_m^0 + T_c) \). The first exponential in eq 2 is related to the diffusion of the polymeric chains from the melt to the crystal front. The second exponent describes the energetic contribution for polymeric chains to form secondary nuclei on the growth front. Thus, the growth can be modeled as the product of two contributions: (i) chain diffusion and (ii) secondary nucleation activation energy.

It is clear from Figure 7 that the incorporation of an increased amount of LNP leads to a further reduction in the growth kinetics of the nanocomposites. While \( G \) is a strong function of temperature (Figure 7a), \( G/G_{\text{PEO}} \) is essentially temperature-independent (Figure 7b). This leads to \( K_g^c \) values that are unaffected by the presence of the LNPs \( (K_g^c/K_g^{c, \text{PEO}} \approx 1, \text{ Figure 8}) \). Thus, LNPs suppress growth kinetics by slowing down the polymeric chain diffusion in the melt (i.e., the first term in the LH model, \( G_0 \exp \left( \frac{-U^*}{R(T-T_c)} \right) \)), while the secondary nucleation mechanism \( (K_g^c) \) is unaffected. These results are in good agreement with previous studies performed on PEO/SiO\(_2\), PEO/PMMA-g-SiO\(_2\), and PE/PE-g-SiO\(_2\) systems. Altorka et al. associated the reduction in the growth kinetics due to the increase in the nanocomposite melt viscosity (\( \eta \)) upon the addition of NPs. It was shown that the chain...
In the latest revisions of the original Lauritzen and Hoffman crystallization theory performed by Hoffman et al., they incorporated the reptation dynamics of macromolecules in an isotropic entangled melt and postulated that the preexponential factor $G_0$ is a function of the inverse of the number of segments within the polymer chain ($n$). Hence, while $U^*$ could be considered proportional to the local chain segmental mobility at the growth front, $G_0$ values depend on the reptation of the entire chain, which is a function of melt viscosity. In the results presented in this section, we show that LNP addition does not influence the local segmental dynamics during secondary nucleation at the growth front, as $U^*$ remains constant. However, lignin-PEO interactions slow down the reptation of the polymer chains with a concomitant melt viscosity increase. In conclusion, the decrease in PEO spherulitic growth rate observed with increasing LNP concentration (Figure 7) can be interpreted as being caused by the slowing down of the global chain dynamics due to PEO-lignin interactions (detected by FTIR in Figure 3).

The extent of confinement imposed by the LNPs can be quantified using different metrics. In this context, we use the ratio of the LNP surface area ($SA_{LNP}$) to the PEO volume ($V_{PEO}$) adopted from Jimenez et al. It was shown that $SA_{LNP}/V_{PEO}$ is an accurate measure of the confinement in each of the PEO/SiO$_2$, PEO/PMMA-g-SiO$_2$, and PE/PE-g-SiO$_2$ systems. For comparison, we replotted $G/G_{polymer}$ of the previously published systems, and superimpose the average $G/G_{PEO}$ values of the PEO/LNP nanocomposites as a function of confinement (Figure 9). (For detailed measurements of $SA_{LNP}/V_{PEO}$, see the Supporting Information.)

Two distinct regimes were observed by Altorbaq et al. as shown in Figure 9: (i) NP-dominated and (ii) brush-controlled regimes. In the brush-controlled regime, growth kinetics are

**Figure 7.** (a) Growth rate ($G$) plotted for each LNP loading. Solid lines correspond to Lauritzen–Hoffman (LH) fits. (b) Nanocomposite growth rate normalized by the neat PEO ($G/G_{PEO}$) at each measured temperature. Solid lines correspond to $G/G_{PEO}$ values averaged over all temperatures, showing how $G/G_{PEO}$ (solid symbols) are scattered away from the corresponding averaged value.

**Figure 8.** Relative change in the secondary nucleation activation energy parameter ($K_G^*/K_{G_{PEO}}$) plotted as a function of LNP content.

**Figure 9.** Relative growth rate change ($G/G_{polymer}$) replotted as a function of confinement ($SA_{LNP}/V_{polymer}$) for each of PEO/SiO$_2$, PEO/PMMA-g-SiO$_2$, and PE/PE-g-SiO$_2$ systems. $G/G_{PEO}$ values for PEO/LNP composite, taken from the averaged values in Figure 7b (solid lines), are superimposed for comparison (red solid circles). Dashed lines correspond to the two general observed regimes: NP-dominated regime (black curve) and brush-controlled regime (red curve). The NP dispersion states of the reported works are shown in the legend as well-dispersed (WD), connected-sheets (CS), strings (S), and aggregated (Agg) structures.
highly suppressed by the chemically bonded chains on the NP, resulting in a strong growth reduction (Figure 9, red curve). Bare and aggregated grafted NPs show a much weaker effect on the growth kinetics denoted as NP-dominated regime (Figure 9, black curve). Clearly, LNPs strongly decrease the growth rate of the PEO, closely tracking the behavior observed in the brush-controlled regime in Figure 9. We ascribe this result to the (strong) hydrogen bonds between the well-dispersed LNPs and the PEO matrix.

3.4. Overall Crystallization Kinetics and Self-Nucleation. 3.4.1. Nonisothermal Crystallization. DSC experiments have been performed to understand the effect of LNPs on overall PEO crystallization kinetics (nucleation and growth). First, we performed nonisothermal crystallization measurements using the heat-cool-heat protocol (see Section 2.7) to evaluate each of the nonisothermal crystallization parameters: \( T_c \), \( T_m \), and \( \chi_c \) (the degree of crystallinity). Figure 10 plots both \( T_c \) (blue) and \( T_m \) (red), as a function of LNP content.

Figure 10. Nonisothermal DSC results showing peak values of the crystallization temperature, \( T_c \) (blue), and melting temperature, \( T_m \) (red), as a function of LNP content.

Next, we evaluate the nucleation efficiency (NE) for the different LNP contents following the Fillon et al. protocol

\[
\%NE = \frac{T_c^{\text{LNP}} - T_c^{\text{PEO}}}{T_c^{\text{max}} - T_c^{\text{PEO}}} \times 100 \tag{3}
\]

where \( T_c^{\text{LNP}} \) and \( T_c^{\text{PEO}} \) are the nanocomposite and neat PEO crystallization temperatures measured from nonisothermal DSC experiments, respectively, and \( T_c^{\text{max}} \) is the maximum crystallization temperature of neat PEO determined at the lowest \( T_c \) of Domain II (see the Supporting Information for more details). Based on NE values, the noncrystallizable components can be characterized as: nucleating (NE = 0–100%), supernucleating (NE > 100%), or antinucleating (NE < 0%) agents. Figure 11 plots NE as a function of LNP content. LNPs are remarkably supernucleating agents for PEO content. Notice that in Figure 11, the value reported for neat PEO corresponds to that of the ideally self-nucleated sample, and hence a value of 100% NE is reported, as in that case \( T_c^{\text{LNP}} \) must be substituted by \( T_c^{\text{max}} \) in eq 3. Once again, aggregation limits supernucleation for an LNP concentration of 20 wt %. Previous works have shown that carbon nanotubes can also be supernucleating agents for PEO, PE, and PCL. This means that the nucleating action of these nanofillers, and in the present case LNPs, can be more efficient than the polymer’s own self-nuclei in triggering heterogeneous nucleation. These results are in very good agreement with nucleation kinetics measured under isothermal conditions (see Figure 6 and compare with Figure 11).

One point to address is that most of the reported nucleating agents have been discussed in terms of nucleation efficiency, where the exact mechanism has not yet been clearly understood. In other NP systems (such as SiO2, graphene sheets, clays), it has been shown that well-dispersed NPs (with favorable NP–polymer interaction) result in better nucleation power, where aggregated structures lead to low NE values. Herein, despite the nucleation mechanism, we show that organic LNPs outperformed commercially available inorganic nucleating agents, providing a renewable, biocompatible replacement.

3.4.2. Overall Isothermal Crystallization Kinetics. Previous works demonstrated that the observed isothermal overall crystallization kinetics (using the DSC) could be dominated by nucleation kinetics in many cases, sometimes by growth. We perform isothermal DSC measurements to understand the contribution of nucleation and growth processes to overall crystallization kinetics. Isothermal exotherms were recorded according to the experimental procedure discussed in Section 2.7. The overall crystallization rates are then estimated by calculating the inverse of the half-crystallization time (1/\( \tau_{50\%} \)). Figure 12a,b compares the corresponding 1/\( \tau_{50\%} \) and [1/\( \tau_{50\%} \)/1/\( \tau_{50\%}^{\text{PEO}} \)] as a function of isothermal crystallization temperature. For comparison, the averaged [1/\( \tau_{50\%} \)/1/\( \tau_{50\%}^{\text{PEO}} \)]
parameter proportional to the primary and secondary nucleation activation energy (denoted with a superscript $\tau$ and is related to both nucleation and growth). Although the extent of enhancement in the overall crystallization rate is dominated by nucleation, $[1/\tau]_{\text{50%}}/\tau_{\text{50%,PEO}}^G$ is temperature-independent tracking the behavior of $G/G_{\text{PEO}}$ in Figure 7b. Previous works have observed a decrease in $K_g^\tau$ upon nucleating agents’ incorporation similar to the observed $\Delta G$ trend in Figure 6. This could be attributed to the minimal changes in growth ($G/G_{\text{matrix}} \sim 1$) for each of the previously studied systems.

In the present case, the values of $K_g^{G}$ and $K_g^\tau$ (reported in the SI) do not significantly vary with filler loading (see Figure 8 and Figure 13). It is possible that the supernucleation effect is

compensated by the strong polymer/filler interactions that cause reductions in growth rates (see associated confinement effects in $G$ reported in Figure 9), leading to such filler-content-independent values of secondary nucleation and overall crystallization energy barriers. It should be noted that all of the constant $K_g^G$ values can be approximated as $1.2 \times 10^5$ K$^2$, while those of $K_g^\tau$ can be approximated to $2.2 \times 10^5$ K$^2$; as expected, the overall crystallization energy barrier is larger by a factor of 2 when the primary nucleation is taken into account together with the growth or secondary nucleation contribution.

To further understand the crystallization process of the PEO/LNP nanocomposites, we fit the experimental data using the Avrami model

\[
1 - V^g_c(t - t_0) = \exp(-k(t - t_0)^n)
\]

where $t$ is the crystallization time, $t_0$ is the induction time, $V^g_c$ is the relative volumetric fraction transformed (crystallized), $k$ is the overall crystallization rate constant, and $n$ is the Avrami index. (Detailed analysis of the Avrami fit is shown in the Supporting Information, Figure S7.) Müller et al. considered $n$ as the sum of two contributions:

\[
n = n_a + n_{gd}
\]

where $n_a$ is the nucleation contribution (instantaneous and sporadic nucleation correspond to $n_a$ values of 0 and 1, respectively) and $n_{gd}$ is the growth dimensionality (usually considered in the range of 1–3, where most unconfined polymers grow into spherulites [3D] or axialites [2D]).
formation). The overall crystallization rate constant \( k \) has units of \( \text{min}^{-n} \). For comparison across different \( n \) values, \( k^{1/n} \) (\( \text{min}^{-1} \)) is then plotted as a function of temperature (Figure 14a), which tracks well with the experimental \( 1/T_{50\%} \) data.

![Figure 14. Avrami fit values of \( k^{1/n} \) (a) and \( n \) (b) plotted as a function of temperature for different LNP contents.](image)

Figure 14b compares \( n \) values for each nanocomposite loading. Clearly, LNP is no significant confinement effect on the overall crystallization process (which includes the competing effects of both nucleation and growth), with \( n \) values greater than 1.5, at least in the composition range employed here (up to 20% loading). This is unlike behaviors observed in nanotube- and sheet-polymer nanocomposites,\(^{66}\) which result in \( n \) values approaching unity but at much higher nanofiller contents. Our results are in good agreement with studies performed on PEO/SiO\(_2\),\(^{67}\) showing unconfined crystals with \( n \) values in the range of \( \sim 3 \) (2.5 can be approximated to 3)—a value corresponding to instantaneously nucleated spherulites or sporadically nucleated axiales. At higher isothermal crystallization temperatures, Figure 14b shows an increase in \( n \) values for the nanocomposite (\( n \rightarrow 3.5 \)). This is related to the occurrence of sporadic nucleation of spherulites when isothermally crystallizing at higher \( T_c \). Similar trends have been observed in previous studies.\(^{34}\)

4. CONCLUSIONS

We thoroughly investigated the crystallization kinetics of PEO/LNP nanocomposites by first morphologically characterizing the dispersion state of LNP in the PEO matrix, then by quantifying the reduction in the growth rate and separately the enhancement in nucleation kinetics. It was found that LNPs tend to disperse well in the PEO matrix, with slight aggregation occurring at larger LNP contents. Such good dispersion is likely related to the strong multiple hydrogen bonds formed between the LNP and PEO, which was confirmed by FTIR measurements. The former argument can also justify the order of magnitude increase in nucleation rates, with supernucleating efficiencies at moderate LNP contents, which tracks the general behavior observed previously for well-dispersed, surface-modified, inorganic NPs. Compared to bare silica NPs, LNPs show a much stronger reduction in the spherulitic growth rate, following a similar trend previously observed for polymer-grafted NP-based nanocomposites. Finally, the overall crystallization kinetics shows similar trends to the nucleation results when measured at very low LNP content. As we further incorporate LNP, the overall kinetics keeps decreasing since the growth kinetics becomes more depressed at higher LNP content. This elucidates the importance of separately measuring each of the growth and nucleation kinetics, where the DSC measurement is a convolution of both kinetics.

- **ASSOCIATED CONTENT**

  - **Supporting Information**
    The Supporting Information is available free of charge at [https://pubs.acs.org/doi/10.1021/acs.macromol.2c00925](https://pubs.acs.org/doi/10.1021/acs.macromol.2c00925).
    - LNP characterization using DLS, AFM, and TEM; deconvolution of the OH band from FTIR analysis; Lauritzen-Hoffman and Turnbull-Fisher parameters evaluation; heating and cooling DSC scans; self-nucleation domains; and Avrami fit (PDF)

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Notes
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