Compatibilized low-density polyethylene/linear low-density polyethylene/nanoclay nanocomposites: II. Opposing effects of nanofiller on quiescent and shear-induced crystallization

Farkhondeh Hemmati | Omid Yousefzade | Hamid Garmabi

Department of Polymer Engineering and Color Technology, Amirkabir University of Technology, Tehran, Iran

Correspondence
Farkhondeh Hemmati, Department of Polymer Engineering and Color Technology, Amirkabir University of Technology, Tehran, Iran.
Email: hematif@aut.ac.ir

Abstract
Isothermal and non-isothermal crystallization processes of polyolefin nanocomposites based on low-density polyethylene/linear low-density polyethylene/nanoclay have been investigated, and the effects of nanoclay loading and dispersion state have been studied. Moreover, the isothermal crystallization of polyethylene chains has been evaluated in the quiescent and shear-induced conditions. In quiescent crystallization, adding 1 wt% nanofiller improves the crystallization rate, whereas an increment in the organoclay loading retards the crystallization process. However, an opposing effect of nanoparticles is observed in the shear-induced crystallization. The findings show that the incorporation of 5 wt% nanoclay in good dispersion state considerably accelerates the shear-induced crystallization process. This influence is found even for very weak shear flow fields. The synergistic effects of nanoclay addition and shear field presence on the crystallization process are of major significance particularly for polyolefin products, which are commonly manufactured by using melt processing methods.

KEYWORDS
blend, crystallization, nanocomposite, polyethylene, shear

1 INTRODUCTION
Blends of linear low-density polyethylene (LLDPE) and low-density polyethylene (LDPE) are of great industrial and academic interest because of their good processability and excellent mechanical properties for packaging film applications. LLDPE is incorporated into LDPE owing to the superior mechanical characteristics. The produced LDPE/LLDPE films are known to have lower haze and enhanced bubble stability. Moreover, blending LLDPE with LDPE enables manufacturers to use the conventional LDPE film-blowing apparatus without any modification for producing LDPE/LLDPE films. Although LDPE and LLDPE polymers are known as the most extremely versatile plastics, their utilizations are restricted due to several drawbacks, such as low strength and stiffness, poor heat resistance, and gas barrier properties particularly in food packaging applications. These drawbacks can be resolved by compounding various inorganic nanofillers especially layered silicate with polyolefins, which has become a well-established strategy through the past decades. The most notable feature of polyethylene (PE) nanocomposites is the considerable property improvement at low loadings of nanofillers on account of the high aspect ratio and at least 1-nanometer size dimension of nanoparticles.

In semicrystalline polymeric microcomposites and nanocomposites, such as PE nanocomposites, the crystallization behavior in quiescent, and shear-induced states, the resultant crystal size, structure, and degree of crystallinity have of the utmost importance as a result of their profound impact on final
morphology and properties.\textsuperscript{71} The crystallization kinetics of PE is tightly controlled by the rate of nucleation and crystal growth stages, which are both affected by the nanofiller presence. Nanoparticle solid surfaces could act as effective heterogeneous nucleating agents that enhance the nucleation and crystallization kinetics, thereby diminishing the crystallization activation energy, increasing the nucleus and spherulite density, and reducing the crystal size.\textsuperscript{8–11} Besides, nanofiller can also bring a physical hindrance to the segmental motion of polymer chains and correspondingly, an increment in the required energy for segmental rearrangements, hence causing a decrease in the crystallization rate, crystallinity weight fraction, and crystal perfection degree.\textsuperscript{9,12} The crystallization behavior of nanocomposites was found to depend on the filler loading and dispersion state in the matrix, which substantially influence the relative dominant status of the mentioned effects.\textsuperscript{10,13,14}

However, almost all processing methods of polyolefin blends and composites such as film blowing, injection molding, extrusion, and fiber spinning involve extensional and shear flow fields on melt. After cooling, the obtained product has a thermo-mechanical history of the preceding melt process, which leads to molecular orientations. Therefore, the nucleation and crystallization behavior is affected by this history even that is provoked by weaker shear deformations.\textsuperscript{15,16} Considering this fact, the study of flow-induced crystallization has great significance for the semicrystalline polymers due to the real conditions of melt processing. In the presence of nanoparticles, two factors can simultaneously accelerate the flow-induced crystallization, i.e., shear-assisted nucleation stemmed from molecular orientation and heterogeneous nuclei provided by nanofiller solid surfaces.\textsuperscript{15,17} These factors were assessed to have synergistic effect on the crystallization kinetics of semicrystalline nanocomposites at high enough shear rates that lead to morphological changes from isotropic spherulites to row-like crystalline structures such as cylindrites and strings of spherulites.\textsuperscript{15,16} The filler influences on shear-enhanced crystallization were reported to be controlled by the geometric shape and surface to volume ratio of particles. The authors stated that at the same conditions, nanofiller can considerably promote the shear-induced crystallization, whereas the micron size filler does not succeed in accelerating this phenomenon.\textsuperscript{18}

In our work, the polyolefin blends of LDPE/LLDPE were chosen and compounded by organically modified nanoclay owing to their wide range of industrial applications through melt-blending processes. In the previous study, the effects of some material variables including clay loading and a processing parameter, namely mixing sequence, on structural, mechanical, and thermal properties of LDPE/LLDPE/nanoclay hybrid nanocomposite were investigated. The findings verified that the addition of organoclay noticeably improves the blend Young modulus, toughness, and thermal stability.\textsuperscript{19} However, in the present research, the crystallization behavior of the used polyolefins is evaluated by using a conventional thermal analysis and small-amplitude oscillatory shear measurements in the presence of nanoclay at different contents and dispersion states. The overall crystallization kinetics is studied by applying Avrami theory and the model proposed by Khanna.\textsuperscript{20} In isothermal quiescent crystallization process, it will be proven that only nanoclay at low contents about 1 weight percent (wt%) can effectively enhance the crystallization kinetics and an increment in the nanofiller loading retards it regardless of nanoparticle dispersion state. Nonetheless, dynamic melt rheology in linear viscoelastic region shows an opposing trend. To the best of our knowledge, it demonstrates for the first time that even very weak shear flow fields can significantly accelerate the isothermal crystallization at higher nanoclay content and good enough dispersion state. Despite that these conditions have been considered as quiescent crystallization state with no shear influences on the crystalline structure development.\textsuperscript{10,21} This finding has great importance to design the melt processes of semicrystalline polymer nanocomposites because of the nanoparticle and induced molecular orientation synergistic and strong effects on the crystallization behavior and final properties.

2 | EXPERIMENTAL PART

2.1 | Materials and sample preparation

Low-density polyethylene (LDPE, LH0075 grade) with density of 0.919–0.922 g/cm\textsuperscript{3}, melt flow index (MFI) of 0.9 g/10 min (190°C, 2.16 kg), and the melting temperature (\(T_m\)) of 111°C was purchased from Bandar Imam Petrochemical Co. (Bandar Imam, Iran).\textsuperscript{22,23} This polyolefin with \(M_w = 1.27 \times 10^5\) g/mol, \(M_n = 1.76 \times 10^4\) g/mol, and a polydispersity of 7.234 has many long-chain branches. The branching number alters from 0 to 11 per chain dependent on the molecular weight but the average branching number is about 9.\textsuperscript{24} Linear low-density polyethylene (LLDPE, 0209AA grade) with density of 0.919–0.921 g/cm\textsuperscript{3}, MFI of 1 g/10 min (190°C, 2.16 kg), and \(T_m\) of 127°C was supplied by Arak Petrochemical Co. (Arak, Iran). This polyethylene with \(M_w = 1.55 \times 10^5\) g/mol, \(M_n = 2.4 \times 10^4\) g/mol, and a polydispersity of 6.5 has many short-chain branches. The number of these branches is about 5 per 1,000 carbon.\textsuperscript{25} Linear low-density polyethylene grafted by maleic anhydride (PE-g-MA, Orevac\textsuperscript{®}18302N) with grafting level of 0.2–2 wt% and MFI of 1.2 g/10 min (190°C, 2.16 kg) was provided by Arkema (Colombes, France) and applied as compatibilizer at content of 6 wt%. Nanoclay (Nanofil\textsuperscript{®} SE3000 garde), pristine bentonite with sodium ion modified by distearyl dimethyl ammonium chloride, was kindly supplied by Süd-chemie Company (Munich, Germany) and used as received without any further surface treatment.
The content of LLDPE in all the prepared samples was 40 wt%. The melt-blending and compounding of samples were carried out by using a lab-scale co-rotating twin-screw extruder manufactured by Coperion Co. (Stuttgart, Germany) (ZSK25, L/D = 40) at temperature profile of 160–190°C at a screw speed of 600 rpm (without addition any commercial heat stabilizer). To attain a good dispersive and distributive mixing of the components, the segmented screws of the extruder consist of different elements: tooth-mixing elements as a kind of gear-type mixing elements; left-handed pitches; large and small right-handed pitches with 2- and 3-flighted elements; kneading blocks having wide, medium, and small discs with right- and left-handed disc orientations; and kneading blocks with no conveying effect.

For melt-compounding process, two different mixing sequences were used. For type 1, all the components were fed into the hopper of twin-screw extruder simultaneously. The virgin blend of LDPE/LLDPE as control sample was also obtained using mixing sequence type 1. For second type of mixing sequence, two-step melt mixing was used. This order of mixing consisted of the preparation of nanoclay/PE-g-MA masterbatch containing 50 wt% of nanofiller at the first step and dilution of the masterbatch by LLDPE and LDPE resins at the second step. Specimens employed for different analytical techniques were obtained using Toyoseiki compression molding machine (Tokyo, Japan) at 180°C under 15 MPa pressure. In the remaining parts, the samples LDPE/LLDPE/ nanoclay nanocomposites will be coded as LLNCxMSy wherein x and y stand for the nanofiller loading and mixing sequence type, respectively. The content of LDPE (wt%) in the samples equals 100 wt% minus (40 wt% of LLDPE plus z wt% of nanoclay plus 6 wt% of PE-g-MA). In other words, wt% (LDPE) = 100 – [40 wt% (LLDPE) + z wt% (nanoclay) + 6 wt% (PE-g-MA)].

## 2.2 Characterization

Differential scanning calorimetry (DSC) was employed to investigate the non-isothermal and isothermal crystallization behavior of PE in the semicrystalline samples using a Mettler Toledo DSC1 calorimeter (Schwerzenbach, Switzerland) under high pure nitrogen gas purge at a flow rate of 80 ml/min. The temperature and heat flow were calibrated using tin and indium standard samples. In the non-isothermal DSC experiments, the samples were heated from –20 to 220°C at a heating rate of 10°C/min and held for 5 min to erase the thermal history, and then cooled down to ambient temperature at a cooling rate of 10°C/min. Finally, the samples were heated again to 220°C at 10°C/min to evaluate the melting behavior of semicrystalline components. For these non-isothermal tests, the experiments were repeated and the standard deviation of crystallization and melting temperatures was less than 0.5°C. Similarly, the standard deviation of melting and crystallization enthalpy was determined to be less than 0.7 J/g. The weight fraction of crystallinity (X_c) was determined using the following equation:

\[ X_c = \frac{\Delta H}{\Delta H_{100\%\text{crystalline}}} \times 100 \]  

where \( \Delta H \) and \( \Delta H_{100\%\text{crystalline}} \) are the fusion heat of sample and the perfect crystalline compound, respectively. \( \Delta H_{100\%\text{crystalline}} \) is calculated according to the mixture rule:

\[ \Delta H_{100\%\text{crystalline}} = \sum_{n=1}^{3} \Delta H_{100\% n} \times \phi_n \]

where \( n \) represents the semi-crystalline components of samples (LDPE, LLDPE, PE-g-MA), \( \phi_n \) is the weight fraction of component \( n \), and \( \Delta H_{100\% n} \) is the melting enthalpy of 100% crystalline nth component as follows: 285 J/g for LDPE,[26] 293 J/g for LLDPE,[27] and 287.3 J/g for PE-g-MA.[28]

The isothermal crystallization behavior of PE was also evaluated by DSC. In this examination, first the samples were heated to 160°C for erasing the thermal history. Second, the samples were isothermally annealed at 160°C for 5 min to allow the melt to become homogeneous, then quickly quenched to 120°C at a high cooling rate of 50°C/min to crystallize the PE phase. Third, the isothermal crystallization of PE chains was completed at maximum time of 60 min. Fourth, without further cooling to room temperature, the samples were heated to 160°C to measure the melting enthalpy.

Dynamic melt rheology as a useful and reliable tool for evaluation of isothermal crystallization has been verified to be more effective than conventional instruments such as DSC.[17,20] To study the isothermal crystallization by means of dynamic rheology, the linear viscoelastic material functions of the obtained samples were characterized by employing small-amplitude oscillatory shear measurements using a Paar-Physica Oscillatory rheometer (Ashland, USA) with parallel plate geometry (diameter of 25 mm; gap of 3 mm) at highly pure nitrogen atmosphere. In this measurement, the test samples were first heated to 180°C, held for 10 min to eliminate the pristine crystalline structures, and then cooled quickly to 120°C. Subsequently, the isothermal crystallization was followed under isothermal time sweep at a linear strain of 1% and low frequency of 1 rad/s. Furthermore, the isothermal dynamic frequency sweeps at a linear strain of 1% were also performed at 150°C to assess the effects of nanoclay dispersion state and polymer–particle interactions on the molecular motions owing to the high sensitivity of melt viscoelastic characteristics to the polymer chain reptation, diffusion, and interfacial phenomena.

For evaluating the nanoclay dispersion state, the height and phase-mode images of the samples were prepared by tapping mode atomic force microscopy (AFM) using a
Dualscope, DME Atomic Force Microscope (Copenhagen, Denmark) equipped with a DS 95-50-E scanner and an alternating-current probe. Besides AFM, X-ray diffraction (XRD) patterns were recorded using a Philips Xpert X-ray diffractometer (Almelo, The Netherlands) with Co Kα tube, scanning from 1° to 10° at a step size of 0.02°. Moreover, crystalline morphology of the samples were observed using a Carl Zeiss Jeonapol (Göttingen, Germany) polarizing optical microscope (POM) equipped with a Linkam THMS600 hot stage (Surrey, UK) under crossed polarizer. A piece of sample was inserted between two cover glasses, heated to 180°C, and squeezed to obtain a thin film. Then, the prepared slices were annealed at 180°C for 5 min to erase the thermal history. Next, the molten samples were rapidly cooled to 50°C, and then, after 5 min, the POM micrographs of samples were obtained. The lens magnification was 20×.

3 RESULTS AND DISCUSSION

3.1 Non-isothermal crystallization

Non-isothermal crystallization is one of the most important melt processing characteristics of semicrystalline polymers owing to the profound impact of this phenomenon on all final properties. The cooling and heating thermograms of the LDPE/LLDPE blend and the obtained nanocomposites are shown in Figure 1. Since LDPE and LLDPE components contain different length of methylene segments and dissimilar side group type and distribution in their backbones, the crystallization and melting curves of the samples have bimodal peaks. This evidence indicates that the polyolefin phases crystallize at different relative rates and phase separation partially happens during cooling and re-crystallization process of melts. However, the appearance of overlapping peaks with closer melting temperatures than pure LDPE and LLDPE (see subsection 2.1) can demonstrate the co-crystallization process and their partial miscibility.\[29\]

![Figure 1](https://example.com/image.png)

The melting and crystallization characteristics of samples are gathered in Table 1. As can be found, the addition of organoclay affects the crystallization behavior of the LDPE/LLDPE blend. The width of crystallization peak is reduced by incorporating nanoclay particles into the blend. One of the plausible reasons of this change is the nanofiller effect on the LDPE/LLDPE miscibility and the solid–liquid phase separation process. While \(T_m\) of polyolefin phases and crystallization temperature \(T_c\) of LDPE component do not alter noticeably, the crystallization temperature of LLDPE diminishes in the presence of nanolayers. The nanoclay solid surface interacts with polyethylene chains and impedes molecular movements, thereby retarding the growth stage of crystallization process.\[10\] Furthermore, the pinning effect of solid nanoparticles and the resultant non-equilibrium compatibilization mechanism of nanoclay along with the equilibrium mechanism can lead to an enhancement in LDPE/LLDPE miscibility and mutual solubility.\[30\] As a result, the diluent role of dissimilar chains and co-crystallization phenomenon become stronger by adding nanoclay layers.

Another notable point in the non-isothermal crystallization results is opposing changes in the relative crystallinity weight fraction \(X_c\). Although the crystallinity degree is relatively lower in the nanocomposite containing 1 wt% nanofiller than the virgin blend, an increment in the nanoclay loading to 5 wt% augments this quantity. Overall, nanoclay filler influences the LDPE/LLDPE crystallization process from different aspects. First, solid nanofiller surface can provide heterogeneous nucleation sites for polymer chains and improve the nucleation and crystallization kinetics. In contrast to the first one, the polymer chains and nanoclay interactions impede the polymer segmental motion and growth stage of crystallization process. The mentioned phenomena have mutually opposite effects on the polyethylene crystallization process and the competition between these two determines the crystallization behavior.\[8,10,21\] In a similar manner to the second aspect, the incorporation of nanolayers has also changed the LDPE/LLDPE miscibility state and mutual solubility. Therefore, the crystallization of each phase is affected more intensely
by the presence of more dissolved chains of the other phase. It seems that the observed increase in $X_c$ by incorporating more nanoparticles results from the stronger heterogeneous nucleation role of solid nanolayers or intense restricted phase separation and the corresponding co-crystallization phenomenon.

However, to study the nanoclay influences on the crystallization process more precisely and to find the predominant action of nanoparticles, the isothermal crystallization behavior of the blend and nanocomposites is evaluated, though LDPE/LLDPE phase separation and miscibility state changes in the presence of nanofiller have not been our priority.

### 3.2 Isothermal crystallization in quiescent conditions

The evolution of crystallization enthalpy versus time for the virgin blend and nanocomposites during quiescent isothermal crystallization process is presented in Figure 2. As it can be easily seen, different loadings and dispersion states of organoclay in the polymer blends have a considerable impact on the kinetics of the quiescent crystallization process. For evaluation of the crystallization kinetics in more detail, Avrami model is used to fit the experimental data. Avrami equation has been known as a useful tool to analyze the whole isothermal crystallization process of polymers including both nucleation and growth stages.\(^{[12,21]}\)

The equation can be written as follows:

$$1 - X_n(t) = \exp(-kt^n)$$

(3)

where $X_n(t)$ is the relative crystallinity degree at crystallization time $t$, $n$ is the Avrami index, and $k$ is the overall crystallization rate constant. While $k$ is dependent on the nucleation and growth kinetics, the exponent $n$ is a function of the growing crystal dimensions and nucleation types, i.e., heterogeneous or homogeneous self-nucleation.\(^{[8]}\) The slope and intercept of $\log[-\ln(1 - X_n(t))]$ versus $\log(t)$ curves are, respectively, equal to the Avrami index ($n$) and $\log(k)$, which are calculated for different samples and collected in Table 2.

Moreover, the crystallization half-time ($t_{1/2}$), the time in which 50% of final crystallinity is obtained, as well as the melting enthalpy is also gathered in Table 2.

As can be found from the data, the quiescent crystallization rate is enhanced by adding 1 wt% organoclay, which is resulted in lower crystallization half-time, smaller Avrami index ($n$), and larger Avrami rate constant ($k$). These changes are most probably caused by the assisted nucleation stage of polyethylene crystallization process in the presence of nanoparticles. Even though self-nucleation phenomenon is a time-dependent process and arises from the segment statistical fluctuations in local order, the solid surface of nanolayers catalyzes the nucleus formation process by providing accessible heterogeneous nucleation sites.\(^{[20]}\) Therefore, the nucleation stage and the whole crystallization process are accelerated by incorporating 1 wt% nanoclay.

However, for LLNC5MS1 sample, increasing the nanoclay loading to 5 wt% leads to an adverse effect on the crystallization process. By applying the same preparation procedure, namely mixing sequence type 1, the addition of higher nanofiller content to matrix worsens the dispersion state of nanoclay and growth stages.\(^{[12,21]}\)

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### Table 1

<table>
<thead>
<tr>
<th>Sample</th>
<th>LDPE phase (°C)</th>
<th>LLDPE phase (°C)</th>
<th>$\Delta H_m$ (J/g)</th>
<th>$X_c$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Virgin blend</td>
<td>95.8 112.0</td>
<td>111.6 124.1</td>
<td>125.8</td>
<td>43.6</td>
</tr>
<tr>
<td>LLNC1MS1</td>
<td>95.6 113.6</td>
<td>110.4 125.7</td>
<td>110.4</td>
<td>38.7</td>
</tr>
<tr>
<td>LLNC5MS1</td>
<td>96.1 113.0</td>
<td>108.3 124.2</td>
<td>119.6</td>
<td>43.6</td>
</tr>
<tr>
<td>LLNC5MS2</td>
<td>96.0 112.1</td>
<td>108.6 124.0</td>
<td>127.1</td>
<td>46.4</td>
</tr>
</tbody>
</table>

### Table 2

<table>
<thead>
<tr>
<th>Sample</th>
<th>$n$</th>
<th>$k$ (s$^{-1}$)</th>
<th>$t_{1/2}$ (min)</th>
<th>$\Delta H_m$ (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LDPE/LLDPE blend</td>
<td>2.05</td>
<td>1.03 × 10$^{-7}$</td>
<td>7.3</td>
<td>12.46</td>
</tr>
<tr>
<td>LLNC1MS1</td>
<td>1.91</td>
<td>9.84 × 10$^{-7}$</td>
<td>3.1</td>
<td>12.33</td>
</tr>
<tr>
<td>LLNC5MS1</td>
<td>6.82</td>
<td>6.92 × 10$^{-22}$</td>
<td>25</td>
<td>9.42</td>
</tr>
<tr>
<td>LLNC5MS2</td>
<td>3.15</td>
<td>1.07 × 10$^{-11}$</td>
<td>19.5</td>
<td>14.86</td>
</tr>
</tbody>
</table>
nanoparticles (for more information on the nanoclay dispersion state in these samples, refer to[19]). According to this reference, the XRD spectrum of LLNC5MS1 sample shows a distinct peak about 2θ of 6.33°, whereas no peak is observed at the scattering angles between 0° and 10° for LLNC1MS1 nanocomposite. The intercalated multilayer stacks of nanoclay in LLNC5MS1 sample can be observed as bright features in the AFM phase-mode images of Figure 3e,f, since the phase contrast images are inferred to be sensitive to surface properties, such as modulus, viscoelastic characteristics, and chemical composition.[19,31] Higher loading of nanofiller along with the intercalated morphology in this sample results in relatively stronger interactions between polymer chains and nanoparticle solid surface. The stronger polymer–particle interactions can be evaluated by rheological experiments owing to the high sensitivity of melt viscoelastic properties to the polymer chain reptation, diffusion, and interfacial phenomena.[30] Figure 4 shows the isothermal frequency sweep results of the blend and nanocomposites at 150°C.

At the terminal zone of the logarithmic modulus-frequency curve for a homopolymer or an unfilled polymer matrix, $G'$ and $G''$ follow the power-law behavior with the slope of 2 and 1 ($G' \sim \omega^2$, $G'' \sim \omega$), respectively.[32] However, the pure blend with heterogeneous binary morphology reveals a gel-like behavior at low frequencies in which $G' \sim \omega^\alpha$. The exponent $\alpha$ equals to 0.82 for the blend. Moreover, the non-terminal behavior of the LDPE/LLDPE blend is intensified by the incorporation of nanoclay especially at 5 wt%.

This exponent is reduced to 0.762, 0.745, and 0.743 for LLNC1MS1, LLNC5MS1, and LLNC5MS2, respectively. The intensified gel-like behavior and modulus rises at low-frequency zone verify the formation of an elastic polymer-filler physical network and nanoparticle-polymer chain interactions.[30] However, the gel-like behavior comparatively heightens for the nanocomposites containing 5 wt% indicating the formation of stronger polymer-filler network and interactions. Because of these interactions, the polymer segmental motions are restricted much more in LLNC5MS1.

![FIGURE 3](image3.png)

**FIGURE 3** Atomic force microscopy (AFM) images of (a–c) LLNC5MS2; (d–f) LLNC5MS1. Left images show height-mode micrographs. Middle and right images show phase-mode micrographs. Arrows mark nanoclay layers. Z-axes are on the right side of images [Color figure can be viewed at wileyonlinelibrary.com]

![FIGURE 4](image4.png)

**FIGURE 4** Storage and loss modulus ($G'$ and $G''$) versus frequency for low-density polyethylene (LDPE)/linear low-density polyethylene (LLDPE) blend and the obtained nanocomposites [Color figure can be viewed at wileyonlinelibrary.com]
sample than the nanocomposite containing 1 wt% filler, and consequently, the growth stage of the quiescent crystallization is retarded more significantly. Another striking outcome of the molecular movement hindrance is the restricted LDPE/LLDPE phase separation during crystallization process. Due to the greater impact of non-equilibrium compatibilization mechanism of nanoclay in LLNC5MS1 and the presence of more dissolved LDPE chains, the isothermal crystallization process of LLDPE phase takes place at lower rate. Because of these phenomena, the crystallization half-life increases and the Avrami rate constant and crystallinity degree diminishes to lower values by raising the organoclay loading. Similar results have been reported by other researches.\cite{8,12,17,33}

At the same nanofiller content, changing the sample preparation method from LLNC5MS1 to LLNC5MS2 sample enhances the quiescent crystallization kinetics, thereby decreasing $t_{1/2}$ and increasing Avrami rate constant. As verified in our previous paper, applying the mixing sequence type 2 improves the dispersion state of nanolayers, which is also assessed by taking a closer look at the AFM phase-mode images of Figure 3. The presence of single layers and stacks with much smaller number of layers that are identified as white features proves better dispersion and larger delamination of nanoclay in LLNC5MS2 sample. Since the overall crystallization rate and accessible nucleation sites are controlled by the geometrical shape and surface to volume ratio of particles, better dispersion of organoclay bring much more accessible heterogeneous nucleation sites and higher nucleation and crystallization rate.\cite{18,20} The improved nucleation kinetics in this sample leads to the largest melting enthalpy as well.

The incorporation of organoclay into the LDPE/LLDPE blend changes the Avrami index $n$ alongside the aforementioned crystallization characteristics. A shift in nucleation mechanism from homogeneous to assisted heterogeneous nucleation is one of the explanations for the Avrami index variations. Another reason for the observed variations is the dimensionality of growing crystals. The formed crystalline structure in the virgin blend is isotropic spherulites, which can be found in the AFM height and phase-mode images shown in Figure 5a,b. Despite this fact, the PE crystalline structures in LLNC5MS2 sample are parallel layers that are discernible as brown features in the two-dimensional phase-mode image of Figure 5c. Owing to the effective role of nanoparticles in providing heterogeneous nucleation sites, some crystals develop from nanoclay solid surface and perpendicular to the polymer-filler interface, thereby forming columnar crystalline layers that are known as transcrystalline structures.\cite{34} The crystal dimension alteration along with the nucleation type in the presence of organoclay layers results in the Avrami index changes. However, the crystallization process with more accessible nucleation sites leads to the formation smaller crystals in larger quantities.\cite{15,18} Although the POM micrographs of Figure 6 seemingly do not have enough magnification, the formation of smaller crystals in the nanocomposite samples particularly in LLNC5MS2 can be perceived.

As mentioned before, most processing methods of polyolefin blends and composites involve melt flow fields. During cooling process, the thermo-mechanical history of the preceding melt process influences the nucleation and crystallization behavior. Thus, it seems essential to conduct an investigation into the isothermal crystallization of the polyolefin blend and nanocomposites in the presence of weak shear deformations.

### 3.3 Isothermal crystallization in shear-induced conditions

Material linear viscoelastic functions are extremely sensitive to the changes in polymer melt structure and can provide useful information on the crystallization behavior of polymer melt under shear flow fields.\cite{17,18} The results of isothermal time sweeps with small frequency and strain, including storage modulus ($G'$) and loss tangent ($\tan \delta$) variation versus time, for the virgin blend and nanocomposites are shown in Figure 7. During isothermal crystallization, the storage modulus demonstrates an unbounded monotonic increase in marked contrast to $\tan \delta$. This increment indicates a gel-like behavior and results from the formed crystallites that act as physical network junction points.\cite{18} The storage modulus of all prepared samples reveals an upturn after a short time and finally reaches a final plateau at long enough experiment time. By considering the crystals as physical cross-links, the observed changes in $G'$ versus time refer to isothermal crystallization kinetics. According to Khanna, the first researcher who testified to the efficacy of rheometry to evaluate the crystallization behavior of polymers, the normalized modulus ($G_n(t)$) can replace the relative crystallinity degree ($X_n(t)$) in Avrami equation\cite{12,18,20}:

$$G_n(t) = 1 - \exp\left(-k^n t^p\right)$$

(4)

where the normalized modulus, $G_n(t)$, is given by:

$$G_n(t) = \frac{G'(t) - G'(0)}{G'(\infty) - G'(0)}$$

(5)

In Equation (5), $G'(t)$, $G'(0)$ and $G'(\infty)$ are storage modulus at time $t$, $t = 0$ and infinity, respectively. By using these equations and plotting log $[-\ln(1 - G_n(t))]$ versus log($t$) as shown in Figure 8, the Avrami index and rate constant are calculated and collected in Table 3. In this table, other related crystallization characteristics including crystallization half-time ($t_{1/2}$) and onset ($t_{onset}$) are also gathered. These values are defined as the time in which 50% and 10% of total $G'$ changes is attained, respectively.

As can be seen from Figures 7 and 8 and the data shown in Table 3, the isothermal crystallization of polyethylene chains recorded by the dynamic time sweep is
not significantly influenced by adding 1 wt% nanoclay. Nonetheless, the Avrami rate constant rises to a larger value for LLNC1MS1 sample proving a slightly higher crystallization rate. Despite the effect of nanoparticles in this sample, an increment in nanofiller content leads to noticeable crystallization process retardation. It is verified by using isothermal frequency sweeps that the polymer-filler interactions intensify in LLNC5MS1 nanocomposite, thereby causing
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a slower crystallization process. As a result, the crystallization half-time and onset comparatively increase and the Avrami rate constant diminishes for this sample. The blend crystallization processes studied by DSC and rheometry are affected in a similar manner for these nanocomposites, though this trend changes for the other one, namely LLNC5MS2 sample.

As can be seen, the incorporation of 5 wt% nanoclay by using the second mixing sequence provokes a higher crystallization rate in the shear-induced conditions, which results in lower $k$, $t_{1/2}$, and $t_{\text{onset}}$. Even though it has been reported that dynamic isothermal sweeps at small frequency and strain do not interfere with the crystalline structure development of polymer, using this method along with the well-dispersed nanoclay particles causes an opposite effect on the blend crystallization process than it is observed in the DSC tests. In the quiescent conditions, the addition of 5 wt% nanofiller retards the crystallization process, while higher crystallization rate is obtained for LLNC5MS2 nanocomposite in the presence of a weak shear field.

One of the key factors in the flow-induced polymer crystallization process is the competition between chain orientation and relaxation.[16] According to de Gennes, the conformation of polymer chains changes from random coil to fully extended chains under shear and relaxation occur at the same time. However, the presence of nanofiller solid surface in polymer and resultant pinning effect augments the effective relaxation time of chains and shear-induced orientation is preserved for a longer time. The results demonstrate that the presence of nanoclay layers at high contents and good dispersion state can notably influence the relaxation of oriented chains under weak shear flow field.

TABLE 3  Kinetics parameters of isothermal dynamic sweeps at 120°C

<table>
<thead>
<tr>
<th>Sample</th>
<th>$n$</th>
<th>$k$ (s$^{-n}$)</th>
<th>$t_{1/2}$ (min)</th>
<th>$t_{\text{onset}}$ (s)</th>
<th>Flow sensitivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>LDPE/LLDPE blend</td>
<td>2.22</td>
<td>$5.21 \times 10^{-7}$</td>
<td>10.75</td>
<td>130</td>
<td>0.68</td>
</tr>
<tr>
<td>LLNC1MS1</td>
<td>1.96</td>
<td>$1.94 \times 10^{-6}$</td>
<td>11.50</td>
<td>132.5</td>
<td>0.27</td>
</tr>
<tr>
<td>LLNC5MS1</td>
<td>2.43</td>
<td>$4.34 \times 10^{-8}$</td>
<td>17.83</td>
<td>330</td>
<td>1.40</td>
</tr>
<tr>
<td>LLNC5MS2</td>
<td>2.10</td>
<td>$4.51 \times 10^{-6}$</td>
<td>5.25</td>
<td>51</td>
<td>3.71</td>
</tr>
</tbody>
</table>

FIGURE 7  (a) Storage modulus and (b) loss tangent evolution versus time at a small frequency of 1 rad/s, linear strain of 1% and temperature of 120°C [Color figure can be viewed at wileyonlinelibrary.com]

FIGURE 8  Plot of $\log[-\ln(1 - G(t))]$ versus $\log(t)$ for isothermal crystallization at 120°C determined from small-amplitude time sweeps [Color figure can be viewed at wileyonlinelibrary.com]
thereby enhancing the chain orientation and crystallization kinetics. The incorporation of nanoparticles into polymer and the presence of even very weak flow fields can have synergistic effect on the crystallization phenomenon. As stated by other researchers, the applied shear rate should be larger than a critical value in order to form stable nuclei and reduce the whole crystallization time in the flow-induced crystallization process.\textsuperscript{[16]} However, by adding nanoparticles the molecular relaxation is affected and induced chain orientation accelerates the crystallization process even in much weaker flow fields.

To evaluate the synergistic effect of nanofiller and applied shear on the crystallization phenomenon, the variable flow sensitivity is used:

\[
\text{flow sensitivity} = \frac{k_{SS}}{k_Q} = \frac{1/f_{1/2}^{SS}}{1/f_{1/2}^Q}
\]

where \( k \) is the overall crystallization constant and SS and \( Q \) superscripts stand for shear-induced and quiescent crystallization conditions, respectively. This variable is calculated for different samples and presented in Table 3. As can be seen, the flow sensitivity of isothermal crystallization is increased by adding 5 wt% of organoclay. For LLNC5MS2 nanocomposite having well-dispersed nanolayers, the highest flow sensitivity is obtained. This just proves that the presence of solid nanoparticles in good dispersion state and at higher contents can considerably improve the crystallization process under weak flow fields. This fact is of great importance for polyolefin melt processes wherein the polymer melt always has a thermo-mechanical history of previous process during crystallization.

\section{CONCLUSION}

In this study, the crystallization process of LDPE/LLDPE blend was investigated in quiescent and shear-induced conditions. The effects of organoclay on the crystallization processes were studied in different dispersion states and loadings. The addition of clay nanoparticles influences the non-isothermal crystallization of LDPE/LLDPE blend in different ways by providing heterogeneous nucleation sites, impeding the crystallization growth stage, and molecular movements besides improving the phase miscibility and mutual solubility. The results of quiescent crystallization process and Avrami analysis show that the isothermal crystallization accelerates by incorporating 1 wt% nanofiller, whereas an increment in organoclay content to 5 wt% retards the crystallization process owing to the restricted molecular motion. At 5 wt% clay loading, the crystallization rate is increased by applying the second mixing sequence and attaining better dispersion state of nanolayers. Even though it is not always possible to perform a second mixing sequence from industrial point of view, the better dispersion of nanoclay and resultant higher crystallization rate can be achieved by using certain additives.

Under very weak shear flow fields, the data obtained for isothermal crystallization process show dissimilar changes by adding nanoparticles. Using Khanna’s theory and Avrami analysis, it is verified that the incorporation of 5 wt% organoclay in good dispersion state could substantially accelerate the crystallization process only if flow fields are present. Although it has been reported that dynamic time sweeps at small frequencies and strains has no effect on the crystalline structure development in polymers, the findings demonstrate that in the presence of nanoparticles, it cannot be correct any more. The addition of nanoclay layers and the presence of weak shear flow fields have synergistic effects on the crystallization process. This is of major significance for polyolefin products, which are often manufactured by melt processing methods. The melt in these processes are always subjected to the thermo-mechanical history of preceding process that considerably influences the crystallization phenomenon and final properties.

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\end{itemize}