An insight into different phenomena involved in continuous extrusion foaming of biodegradable poly(lactic acid)/expanded graphite nanocomposites

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The continuous extrusion foaming of poly(lactic acid) (PLA) has several critical drawbacks that crucially limit the substitution of the renewable foams for the extruded foams based on synthetic plastics. In this work, the foamability of PLA melt through a twin-screw extrusion process was improved by using expanded graphite (EG) nanoplatelets having different aspect ratios and loadings along with an organic peroxide. Morphological observations demonstrated the beneficial influences of adding nanofiller, which resulted in the formation of microcellular foams with larger void content and cell densities. Different phenomena, which are involved in the extrusion foaming of PLA melt, are considerably affected by the presence of EG including rheological behavior, PLA crystallization, thermal chain scission of the matrix, chain extension function of the peroxide and thermal decomposition of foaming agent. To correlate the phenomena affected by EG nanofiller with foam morphology, the linear viscoelastic responses, molecular weight, crystallization kinetics and structural properties of PLA and PLA/EG nanocomposites were evaluated.

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1. Introduction

In last decade, much effort has focused on the replacement of synthetic polymers from fossil fuels by renewable and biodegradable polymers from natural resources owing to rising concerns about environmental degradation [1,2]. Poly(lactic acid) (PLA) is a renewable biopolymer produced from corn, rice, wheat, potato, sugar cane and bagasse [3,4]. As a thermoplastic aliphatic polyester, PLA has attracted great attention for biomedical applications including tissue engineering and drug delivery due to the superior biocompatibility, hydrolysis ability and the absence of toxic gas emission during the synthesis process [5,6]. Additionally, PLA has been employed in packaging applications because of its good processability. It can be shaped into films and foams through conventional plastic processing techniques such as extrusion and injection molding [3,7]. PLA foams can potentially replace the common polyethylene and polystyrene foams in packaging industries owing to the accessibility of raw materials, economical synthesis process, good mechanical performance and excellent biodegradability [8].

Polymer foaming is carried out through both physical and chemical foaming processes. In physical foaming, a supercritical gas such as nitrogen or carbon dioxide is inserted into the PLA melt, whereas the chemical foaming prerequisite is the incorporation of an exothermic or endothermic foaming agent into the polymer matrix. The thermal decomposition of the foaming agent is accompanied by the evolution of gas molecules that are involved in the bubble formation. Commercially, chemical foaming processes are applied more frequently owing to the considerable cost of a high pressure gas reservoir and pressure control difficulties in the physical foaming processes [9–11].

In spite of the advantages of PLA foams, there are some drawbacks that must be overcome to permit the commercialization of these biodegradable and renewable foams. Poor melt strength, slow crystallization kinetics and low operating temperatures are included. In the foaming process, the low melt strength of PLA has an adverse effect on cell growth and often causes cell wall rupture. One of the commonly used solutions is the addition of a chain extender [12]. In the molten state, the chain extender additive reacts with the hydroxyl or carboxyl end groups of PLA chains and transforms the linear PLA chains to long chain branched macromolecules having higher molecular weight and melt strength. The common chain extender additives have functional groups such as amines, anhydride, carboxylic acid, isocyanate and epoxy groups [13–15]. The resultant branched chain structures give the melt higher strength in the foaming process, wherein the melt is exposed to a biaxial extensional deformation in the cell growth stage [16]. The processing aids based on epoxide groups have high efficiency in the
chain extension reaction and strongly improve the rheological properties of PLA melt. This permits the generation of lightweight foams with more uniform cell structure [17–20].

Because of the high price of common chain extenders, other additives have been recently applied to restrict the impacts of PLA chain scission and molecular weight drop in the continuous foaming processes. One of them is a thermal radical initiator for chain polymerization reactions. Reportedly, the addition of radical initiators can beneficially lead to chain extension reactions of biodegradable polymers, especially PLA [21–26]. The chemical reactions induced by the initiators mostly involve in the formation of longer chains and more long branch branched molecules. The foamability of PLA can be improved by accelerating PLA crystallization as well. Considering the continuous extrusion foaming of a semi-crystalline crystallizer, the crystallization process occurs concurrently with the bubble formation. Crystalline structures as physical junctions of polymer chains can increase the strength of the cooling melt [1,8,12]. The PLA crystallization rate has been enhanced by melt-blending of PLA with another polymer having higher melt strength and crystallization rate [27,28]. Moreover, the melt–compounding of PLA containing micron- or nanometer-sized fillers has been reported [29–31]. The presence of nanoparticles can accelerate the crystallization phenomenon of PLA by providing heterogeneous nucleation sites. Furthermore, the nanoparticles can result in higher melt strength by the absorption of the chains onto solid surfaces and restricting polymer molecular movements. In the foaming process for a polymeric nanocomposite, the presence of nanoparticles can also facilitate the bubble nucleation, by which the cell density maybe increase to larger values [32,33].

In this work, efforts have been particularly made to improve the foamability of PLA melt in a continuous twin-screw extrusion process by incorporating economical additives including an organic peroxide, expanded graphite (EG) nanoplatelets (at different aspect ratios and loadings), a chemical foaming agent (CFA) and a CFA activator. The advantages of EG over other inorganic nanomaterials are the simultaneous improvements of PLA properties such as electromagnetic interference (EMI) shielding property, electrical conductivity, thermal stability and flame retardancy, non-dripping property and char formation, PLA crystallization rate, bubble nucleation rate, foam expansion and limited oxygen index value [34–36]. To get more insight into the morphology evolution for the semi-conductive biodegradable PLA foams, the molecular structure and weight, crystallization kinetics, viscoelastic responses and microstructure have been investigated. A comprehensive understanding of the concurrent phenomena in the continuous extrusion foaming of PLA/graphite nanocomposites including PLA chain scission, chain structural changes, crystallization, EG nanofiller mixing and bubble nucleation and growth has been the main objective of the present study.

2. Experimental part

2.1. Materials

The used PLA (Ö5 BİOKAS grade) with glass transition temperature (Tg) of 60.4 °C, melting temperature (Tm) of 146.8 °C and melt flow index of 7 g/10 min (210 °C, 2.16 kg) was purchased from Chemie Kas (Austria). Two types of graphite powder (104206 and 1.04206sk4206 grades) with primary particle size <50 and 90 µm were prepared by Merck (Germany) and SinChem Co. (South Korea), respectively. The third type of graphite was in the form of flakes with a primary particle size of 500 µm that was purchased from Shandong Qingdao (China). Nitric and sulfuric acids used in the preparation of expanded graphite were obtained by Tehran Kimiya Acid (Iran). The used CFA was azodicarbonamide (7000 dB) supplied by Kum Yang (South Korea). The thermal free radical initiator, namely benzoyl peroxide (BP), as a processing aid and zinc oxide (ZnO) as the CFA activator were supplied by Merck (Germany).

2.2. Sample preparation

To obtain EG nanofiller, firstly graphite particles were intercalated by a mixture of nitric and sulfuric acids. That way, 10 g of graphite was mixed with 200 mL of sulfuric acid, and then 100 mL of nitric acid was slowly added to the mixture that was cooled by an ice-water bath. Secondly, the intercalated graphite particles were separated from the acidic mixture and repeatedly washed with distilled water. Thirdly, the prepared graphite was dried in a vacuum oven at 60 °C for 24 h. Finally, EG was obtained by sudden evaporation of the acids using an electric furnace with a temperature of 1000 °C for the exposure time of 30 s. By thermal expansion, nanofillers with larger volume/mass ratios were prepared.

In order to increase the melt strength of PLA, PLA/EG masterbatches at EG loading of 20 phr were obtained by using a co-rotating twin-screw extruder (Rondol microcompounder, UK) at a screw speed of 150 rpm and a temperature profile of 165, 160, 170, 175 and 175 °C. Before melt-compounding, PLA and EG was dried in a vacuum oven at a temperature of 60 °C for 12 h. The masterbatches were pelletized using a rote-shaped die, cooling water bath and pelletizing machine.

The PLA-based foams were obtained by mixing a certain amount of PLA/EG masterbatch, neat PLA, CFA, ZnO and BP using the twin-screw extruder at a temperature profile of 140, 145, 160, 155, 155 °C and a screw speed of 150 rpm (The processing parameters were chosen based on the results of our prior optimization.). The raw materials of the foaming process were dried in a vacuum oven at 60 °C for 12 h. The formulations of different PLA/EG foams were shown in Table 1. In addition to the prepared foams, the unfoamed nanocomposites were obtained at same formulations without using CFA and ZnO chemicals. Furthermore, the PLA/BP foam and the corresponding unfoamed sample (with UPbla/BP code) were extruded as control samples. In the defined sample codes in Table 1, “F” and “UF” letters at the beginning of the codes show the foam and unfoamed samples, respectively. The “α” letter at the end of a code stands for the EG type. “S”, “M” and “L” letters instead of “α” are the abbreviations of “small”, “medium” and “large” words, which show the EGs obtained from SinChem, Merck and Shandong Qingdao companies, respectively. These letters were opted to define the graphite type owing to the differences in the EG size and aspect ratio, which will be discussed in the following section.

2.3. Characterization

The density of the obtained foams was measured following ASTM D1622 and the density of the unfoamed samples was determined using solvent displacement method according to ASTM D792 standard. Normal hexane with a density of 0.659 g·cm⁻³ at 25 °C was applied as solvent. The void content of the foams was determined according to ASTM D2734 standard following Eq. (1).

\[ V_f = \frac{d_{un} - d_f}{d_{un}} \times 100 \] (1)

Table 1

<table>
<thead>
<tr>
<th>Sample code</th>
<th>PLA (phr)</th>
<th>EG (phr)</th>
<th>CFA (phr)</th>
<th>ZnO (phr)</th>
<th>BP (phr)</th>
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<tr>
<td>FPLA11EGz0</td>
<td>100</td>
<td>1</td>
<td>4/0</td>
<td>0.25/0</td>
<td>0.5</td>
</tr>
<tr>
<td>FPLA13EGz0</td>
<td>100</td>
<td>3</td>
<td>4/0</td>
<td>0.25/0</td>
<td>0.5</td>
</tr>
<tr>
<td>FPLA15EGz0</td>
<td>100</td>
<td>5</td>
<td>4/0</td>
<td>0.25/0</td>
<td>0.5</td>
</tr>
<tr>
<td>FPLA17EGz0</td>
<td>100</td>
<td>7</td>
<td>4/0</td>
<td>0.25/0</td>
<td>0.5</td>
</tr>
<tr>
<td>FPLA19EGz0</td>
<td>100</td>
<td>9</td>
<td>4/0</td>
<td>0.25/0</td>
<td>0.5</td>
</tr>
<tr>
<td>FPLA11Eg0/UFPLA11Eg0</td>
<td>100</td>
<td>11</td>
<td>4/0</td>
<td>0.25/0</td>
<td>0.5</td>
</tr>
<tr>
<td>FPLA13Eg0/UFPLA13Eg0</td>
<td>100</td>
<td>15</td>
<td>4/0</td>
<td>0.25/0</td>
<td>0.5</td>
</tr>
<tr>
<td>FPLA15Eg0/UFPLA15Eg0</td>
<td>100</td>
<td>20</td>
<td>4/0</td>
<td>0.25/0</td>
<td>0.5</td>
</tr>
</tbody>
</table>
where \( V_f \) and \( d_f \) are respectively void content, density of unfoamed and foam samples. The structures of graphite particles before and after thermal expansion as well as the morphology of foams were investigated by scanning electron microscopy (SEM) (AIS2100 model from Seron Technologies (South Korea) and LMU model from Vega Tescan (The Czech Republic)). The structural characteristics of the foams were determined using Digimizer software. The number-average diameter (\( D_n \)) and volume-average diameter (\( D_v \)) of bubbles along with the cell density (\( N_c \)) are given by the following equations:

\[
\begin{align*}
D_n &= \frac{\sum(n_i d_i)}{\sum n_i} \\
D_v &= \frac{\sum(V_i d_i)}{\sum V_i} \\
N_c &= \frac{3 \left( \frac{d_{\text{min}}}{d_f} \right)^2}{\left( \frac{N_i}{A} \right)}
\end{align*}
\]

where \( n_i \) and \( V_i \) are the number and volume of ith bubble with a diameter of \( d_i \), respectively. \( n \) is representative of the cell number in the cryofractured surface of foam with an area of \( A \) [32,37].

The isothermal crystallization kinetics of PLA in the presence of graphite layers was evaluated by using Mettler Toledo differential scanning calorimetry (DSC) (DSC1 model, Switzerland). The samples with a constant weight of 5–10 mg were heated up to 180 °C with a heating rate of 10 °C/min and held for 5 min for erasing the thermal history. Afterwards, the samples were quenched to 118 °C and isothermally kept at 118 °C to complete the isothermal crystallization process of PLA chains. The temperature for isothermal DSC tests was opted based on the non-isothermal DSC experiments. All DSC tests were carried out under highly pure nitrogen atmosphere with a volume rate of 80 mL/min. Temperature and time of the DSC instrument were periodically calibrated by applying tin and indium standard samples. The linear viscoelastic responses of PLA matrix in the presence of EG nanoplatelets were studied by the isothermal oscillatory frequency sweep tests at a temperature of 170 °C and a linear strain of 1%. An Anton Paar parallel plate rheometer (MCR30, Austria) with a constant gap of 1 mm and plate diameter of 25 mm was employed. To avoid thermal degradation and moisture uptake of samples, the sweep tests were conducted under highly pure nitrogen atmosphere. To evaluate the shear-induced crystallization kinetics of PLA chains in the presence of EG, the samples were heated to 180 °C and held for 5 min. Then, the molten samples were quenched to 135 °C and isothermally subjected to shear stress by performing rotational motion at a fixed shear rate of \( 1 \text{ s}^{-1} \) for 10 s. Afterwards, the isothermal oscillatory time sweeps were conducted at a linear strain of 0.5% and small frequency of 1 rad·s\(^{-1}\).

The number- and weight-average molecular weight of PLA chains in the presence of BP and graphite nanofillers were measured by using gel permeation chromatography (GPC, Agilent, USA) after dissolving the samples in tetrahydrofuran. The gel content of PLA foams was determined by putting a dried sample in chloroform solvent for 48 h following Eq. (5).

\[
\text{gel content (\%) } = \frac{W_g}{W_i} \times 100
\]

where \( W_g \) and \( W_i \) are the weight of dried samples after and before dissolving in chloroform solvent, respectively.

3. Results

As a nanocomposite, the aspect ratio, particle size and interlayer spacing of EG nanofiller have profound impacts on the foam microstructure and performance [1,18]. The SEM micrographs of the used graphite nanoparticles before and after thermal expansion are shown in Fig. 1. The graphite flake (EGL) has largest primary size before the thermal expansion. The multilayer stacks as well as single nanoplatelets of flake are evident in the image of Fig. 1(b), which shows the EGL particles after thermal expansion process. The white arrow in the image shows the presence of single nanolayers in the EGL nanofiller. The average diameter and aspect ratio of EGL nanoparticles after thermal expansion was respectively 48.2 ± 14.1 μm and 19.5 ± 7.6. The SEM image of EGM in Fig. 1(d) is also verifies the effective thermal expansion of this graphite type as well. The multilayer graphite stacks with larger d-spacing (marked by white arrow) and single nanoplatelets are clearly observed in the image. The average diameter and aspect ratio of EGM nanoparticles after thermal expansion was respectively 46.2 ± 4.8 μm and 8.9 ± 1.0. In contrast to these types of graphite nanofillers, the common worm-like structure of expanded graphite was not observed at all for EGS. The smallest volume change after thermal expansion belongs to EGS type. The expansion of EGS is not discernable in the related SEM images even at high magnifications. The small EGS particles had average diameter and aspect ratio of 1.5 ± 0.3 μm and 12.3 ± 2.5, respectively. Differences in the morphology of the used EG nanofillers along with the nanoparticle size and aspect ratio inevitably influence the foamability of PLA/EG nanocomposites.

As the key property of foams, the density of unfomed PLA/EG nanocomposites and the corresponding foams was measured and the void content of foams was determined following the Eq. (1). The results are shown in Fig. 2. Overall, adding more nanofiller into the PLA/BP matrix up to 20 phr brings about a noticeable reduction in the void content of the PLA/EG nanocomposite foams. The highest void contents are comparatively measured for FPLA1EGM and FPLA3EGM samples. The other PLA/EG foams do not have larger void content than the control sample, i.e. PLA/BP foam. At constant loading of EG nanofiller, the largest void contents are relatively shown by the PLA nanocomposites containing EG nanoparticles with medium aspect ratio. It was unpredictable, since the strongest activity of EG particles in providing the heterogeneous nucleation sites of bubbles was expected for the largest particles having highest aspect ratio at a constant EG loading. It reveals that other influential factors play a role in controlling the foaming process of PLA/EG nanocomposites as well, which will be discussed. The void content of PLA/EG foams containing the largest EG particles is close to the void content of PLA/EGS foams, at lower EG loadings. The presence of EGL particles just at the highest levels results in the void content similar to the PLA/EGM foam. However, for most cases, the smallest void contents are measured for PLA/EGS nanocomposites, wherein the nanoparticles have the lowest particle size.

To study the influences of graphite size and loading on the cellular structure of the biodegradable foams, the SEM images of the cryofractured surface of the PLA/EG foams and control sample were obtained and represented in Figs. 3 and 4. The related data, \( D_n \) and \( D_v \), are gathered in Table 2.

Considering the SEM micrographs, it is clearly evident that the PLA/BP foam has larger bubbles with a non-uniform cell size distribution comparing with the PLA/EG foams. This microstructure is related to homogeneous cell nucleation without the presence of an external nuclei and low melt strength. The average cell size of the nanocomposites and PLA/BP sample is in the micrometer range and the cell densities are in the scale of \( 10^5 \) cell \( \text{cm}^{-3} \), which are in the common range of PLA chemical foams [7,38]. For most PLA/EG foams, the graphite platelet presence decreases the bubble size and increases the cell density. These observations are even valid for FPLA20EG and FPLA20EGS. The highest cell density in the range of \( 10^6 \) cell \( \text{cm}^{-3} \) belongs to FPLA1EGM sample. Besides, the data in Table 2 reveals that the presence of EG nanofillateis in the PLA matrix at different loadings from 1 to 20 phr reduces the number-average cell size of the control sample, PLA/BP foam. For all PLA/EGS and PLA/EGL nanocomposite foams, the number- and volume-average cell size are smaller than the ones of neat PLA/BP foam. In most of
cases, particularly for the foams containing EGL and EGS, the cell size distribution is comparatively narrower. For instance, the cell size distribution of FPLA20EGL and FPLA20EGS is considerably more uniform than the PLA/BP foam.

Generally, by adding more EG nanoplatelets, the number-average cell diameter diminishes to lower values at first, then increases. The other structural characteristic of the foams, namely, cell density, shows an extremum at lower EG loadings and an increment in the EG content reduces the bubble densities. The maximum value of cell density is attained at 1 phr of EGM among the PLA/EGM foams. Despite this fact, the largest cell densities are obtained at 7 phr of EGL and 5 phr of EGS for the prepared PLA/EGL and PLA/EGS foams, respectively.

A study on the effects of EG type on the foam structural characteristics reveals that the highest cell density and smallest bubble size belongs to the PLA/EGM foams at filler loadings of 1 and 3 phr. However, at higher nanofiller levels, the EGL containing PLA foams have largest cell densities and lowest \( D_{50} \) among different EG types at fixed nanofiller loadings. For instance, at constant nanofiller contents of 7 and 9 phr, the PLA/EGL foams have largest cell densities and smallest bubble size among other foams containing EGS and EGM nanofillers. The presence of smallest particles, EGS, does not lead to the formation

Fig. 1. SEM micrographs of the used graphite nanoparticles: (a) and (b) EGL, (c) and (d) EGM, (e) and (f) EGS; The left and right columns show the graphite nanoparticles before and after thermal expansion, respectively.
of PLA/EG nanocomposite foams with comparatively higher cell densities and smaller bubbles. However, at EG loading of 20 phr, the FPLA20EGS foam shows relatively largest cell density and smallest cell size among others.

In addition to the mentioned results, the SEM micrographs along with the light yellow color of PLA/BP foams clarify the incomplete decomposition of the used chemical foaming agent in the applied extruder barrel temperatures. It has been reported that the decomposition temperature of azodicarbonamide diminishes to the temperature range of 150–190 °C by incorporating zinc oxide activator [39]. However, the decomposition reaction of CFA is controlled by the melt temperature during the extrusion process. The presence of EG nanoparticles affects the extrusion foaming of PLA through several ways such as changing the viscoelastic properties and shear viscous heat of the melt [40].

4. Discussion

The presence of EG nanoparticles in the PLA melt during extrusion chemical foaming process impacts the foamability of PLA chains and the corresponding foam morphology through several phenomena. One of the most pronounced impacts is the heterogeneous nucleation sites provided by the EG surfaces similar to most carbeneous nanofillers [1,41,42]. Another one is the changes in the rheological responses of PLA matrix phase that is of great importance during the growth stage of bubbles [8]. In addition, EG nanoplatelets affect the extent of chemical reactions occurred during the chemical foaming process of PLA including the CFA decomposition, BP radical reaction and PLA chain scission. Furthermore, by passing over the extruder die and cooling process of the extrudate, the non-isothermal crystallization kinetics of PLA chains is influenced by adding EG. All of these phenomena are controlled by the EG aspect ratio and particle size as well as EG distribution and dispersion state [1,8,12]. The observed changes in the structural properties of the PLA-based foams are resulted from the concomitant effects of nanoparticles on the bubble nucleation stage, PLA rheological and crystallization behavior, PLA chain structure and molecular weight and the decomposition reaction extent of CFA and BP. Overall, the one-step continuous extrusion foaming process of PLA melt in the presence of a chemical foaming agent, an organic peroxide and multi-layer EG stacks has great complexities and needs to get insight into the concurrent phenomena very well. In the following part, the observed changes in the PLA/EG foam morphology will be correlated to the mentioned phenomena.

4.1. Heterogeneous bubble nucleation of EG nanoplatelets

To evaluate the effects of graphite presence, dispersion state and size on the PLA foam morphology, the SEM images of the cryo-fractured surfaces of the EG/PLA nanocomposite foams were obtained and shown in Fig. 5. One of the profound impacts of graphite nanoplatelets on the foaming process is the effective role of them in providing heterogeneous nucleation sites for bubbles [41]. As can be found in Fig. 5, the graphite surfaces act as the bubble nucleation sites. Some of them are marked by white arrows in Fig. 5(a)–(g). The positive effect of graphite nanoparticles on the foaming process is also reported by other groups [41,43]. Taking a closer look at the SEM images reveals that the bubbles are formed on the base surfaces as well as the lateral areas of EG particles. Fig. 5(a) demonstrates the nucleation of a bubble on the edge of EG platelets, albeit most of the bubbles are nucleated on the main surfaces of EG particles. The graphite platelets are considerably effective in the foam nucleation stage owing to the large aspect ratio and layered structure [41]. The assisted multi-nucleation influence of EG particles is also probable. In other words, each graphite particle can nucleate more than one bubble concurrently [41]. The cell multi-nucleation role of all used graphite types here are clearly obvious in the PLA matrix in Fig. 5(c), (e) and (f).

The assisted bubble nucleation results in the formation of PLA foams with smaller cells and larger bubble densities. The main reason of the formation of PLA foams with smaller cells in larger quantities and more uniform cell size distribution, particularly at lower EGL and EGM loadings, is most likely the effective role of EG platelets in providing the cell heterogeneous nucleation sites. As can be observed in the SEM images of Fig. 1, the EGM and EGL platelets have comparatively larger expansions and interlayer spacing by the acid intercalation and thermal shock processes. The larger d-spacing of EG platelets brings about a
better dispersion and delamination state of nanolayers in the melt-compounding process, hence increasing the matrix-filler interfacial area and accessible heterogeneous nucleation sites. Nonetheless, the addition of more nano-filler to the PLA matrix reduces the beneficial effect of EG platelets in the cell nucleation stage of foaming process. By increasing the nanofiller loading and reaching the filler percolation threshold, the delamination of EG nanoplatelets in the PLA matrix worsens and more EG aggregates and agglomerates can be formed or remained in the matrix after extrusion processing [41,44,45]. The presence of filler aggregates and EG stacks with more nanoplatelets leads to
Fig. 4. SEM micrograph of the cryofractured surface of the PLA/BP, PLA/EGS and PLA/EGL foams: (a) PLA/BP, (b) FPLA1EGL, (c) FPLA3EGL, (d) FPLA5EGL, (e) FPLA7EGL, (f) FPLA9EGL, (g) FPLA20EGL, (h) FPLA1EGS, (i) FPLA5EGS, (j) FPLA9EGS and (k) FPLA20EGS.

Table 2
Number- and volume-average cell size ($D_n$ and $D_v$) and cell density of PLA/BP and PLA/EG foams.

<table>
<thead>
<tr>
<th>Foam sample</th>
<th>$D_n$ (μm)</th>
<th>$D_v$ (μm)</th>
<th>$N_c \times 10^{-5}$ cell cm$^{-3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PLA/BP foam</td>
<td>20.8 ± 10.0</td>
<td>73.7 ± 20.3</td>
<td>2.33 ± 0.12</td>
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<tr>
<td>FPLA1EGM</td>
<td>20.1 ± 8.30</td>
<td>106.1 ± 32.0</td>
<td>23.2 ± 2.20</td>
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<tr>
<td>FPLA3EGM</td>
<td>17.1 ± 9.00</td>
<td>124.1 ± 28.3</td>
<td>4.08 ± 0.15</td>
</tr>
<tr>
<td>FPLA5EGM</td>
<td>14.1 ± 7.30</td>
<td>55.2 ± 15.5</td>
<td>2.79 ± 0.17</td>
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<td>FPLA7EGM</td>
<td>15.2 ± 9.30</td>
<td>65.0 ± 20.7</td>
<td>3.86 ± 0.31</td>
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<td>FPLA9EGM</td>
<td>15.5 ± 10.4</td>
<td>61.5 ± 24.2</td>
<td>4.35 ± 0.25</td>
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<tr>
<td>FPLA11EGM</td>
<td>15.5 ± 8.70</td>
<td>34.4 ± 12.4</td>
<td>4.92 ± 0.12</td>
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<tr>
<td>FPLA13EGM</td>
<td>19.9 ± 10.4</td>
<td>114.5 ± 34.0</td>
<td>1.61 ± 0.28</td>
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<tr>
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<td>111.8 ± 36.2</td>
<td>1.56 ± 0.32</td>
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<tr>
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<td>44.6 ± 12.5</td>
<td>1.64 ± 0.24</td>
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<td>50.6 ± 29.4</td>
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<td>FPLA9EGL</td>
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<td>30.7 ± 16.3</td>
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<tr>
<td>FPLA20EGL</td>
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<td>22.5 ± 10.2</td>
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<tr>
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<td>2.48 ± 0.23</td>
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<tr>
<td>FPLA5EGS</td>
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<td>42.5 ± 20.5</td>
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</tr>
<tr>
<td>FPLA9EGS</td>
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<td>30.9 ± 13.4</td>
<td>1.38 ± 0.16</td>
</tr>
<tr>
<td>FPLA20EGS</td>
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<td>32.6 ± 16.1</td>
<td>2.84 ± 0.26</td>
</tr>
</tbody>
</table>
smaller PLA matrix/EG interfacial area, thereby less accessible heterogeneous nucleation sites. Consequently, the void content and cell density of the PLA/EG foams diminish and the corresponding average cell diameter increases at larger EG levels owing to the poor dispersion state of nanoparticles at higher loadings. The presence of multilayer EG stacks and nanofiller agglomerates is evident in Fig. 5, especially Fig. 5(g), (h) and (i). The EG nanofillers affect the PLA foaming process not only by the assisted nucleation function, but also by changing the rheological properties of the PLA melt.

4.2. PLA viscoelastic responses in the presence of EG nanoplatelets

After exiting the extrusion die, the bubble nucleation and growth stages begin in the PLA molten state, which clarifies the importance of

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Fig. 5. SEM images of the cryofractured surface of PLA foams containing BP: (a) FPLA5EGL, (b) FPLA5EGM, (c) FPLA5EGS, (d) FPLA9EGL, (e) FPLA9EGM, (f) FPLA9EGS, (g) FPLA20EGL, (h) FPLA20EGM and (i) FPLA20EGS.
rheological behavior of melt. Undoubtedly, the nanofiller presence impacts the PLA rheological properties. The linear viscoelastic responses of the unfoamed PLA/BP sample and PLA/BP/EG nanocomposites at constant EG loading of 3 phr are evaluated by isothermal frequency sweep test. Some of the data are shown in Fig. 6. As can be seen, by adding the EG nanoplatelets, the storage and loss modulus \( (G', G'') \) of PLA melt change, particularly at low frequency region of the curves. These changes verify that the graphitic dispersion and distribution state profoundly impact the molecular motions and relaxation times of PLA chains. By the absorption of PLA chains on the EG surfaces and penetration of the macromolecules into the EG galleries, the entropy of PLA molecules reduces and correspondingly, the relaxation time of PLA chains increases [46]. These effects can be investigated by evaluating the solid-like behavior and relaxation time of the PLA melt [47].

One may know that the extrusion process has a low efficiency as a pump and large portion of the consumed machine power converts to heat, which increases the melt temperature [40]. The presence of solid EG nanoplatelets, particularly at good dispersion and distribution state, substantially affects the chain conformation changes, relaxation phenomena, melt viscosity and system friction [10]. As a result, the EG presence leads to higher shear viscous heat at certain processing conditions, hence increasing the melt temperature. Since PLA has low melt strength for foaming process, the barrel temperature profile was opted to be 160–175 °C, which was low to complete decomposition of chemical foaming agent. The yellow color of the obtained PLA foams confirms that. However, the addition of EG platelets, especially at larger aspect ratio and loading, raises the melt temperature and intensifies the decomposition reaction of CFA. Therefore, larger amount of gases would be released in the extrusion foaming of PLA/EG compounds. One of explanations for the attainment of PLA foams with noticeable cell densities at large EG loadings such as 15 and 20 phr is the positive influence of EG on the PLA rheological properties and CFA decomposition reaction.

Among different EG types, EGS nanoplatelets have smallest aspect ratio and interlayer spacing. Because of poor dispersion state of EGS, the nanofiller adversely impacts the viscoelastic responses of PLA melt (See the data of Fig. 6 and Table 3.). Consequently, the positive effects of EG nanoplatelets on the CFA decomposition reaction, PLA melt strength, gas removal and heterogeneous cell nucleation are less considerable for EGS. Therefore, PLA/EGS nanocomposites have comparatively lower void contents.

![Fig. 6.](image-url)  
(a) Storage modulus \( (G') \) and (b) loss modulus \( (G'') \) versus frequency \( (\omega) \) for some of the unfoamed samples measured at a temperature of 170 °C and a linear strain of 1%.

---

Table 3

<table>
<thead>
<tr>
<th>Sample</th>
<th>( a )</th>
<th>( b )</th>
<th>( \omega_0 )</th>
<th>( \tau_\eta )</th>
<th>( \eta_0 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>UFPLA/BP</td>
<td>1.44</td>
<td>0.93</td>
<td>152</td>
<td>6.6 × 10^3</td>
<td>3907.5</td>
</tr>
<tr>
<td>UFPLA3EGM</td>
<td>1.15</td>
<td>0.93</td>
<td>148</td>
<td>6.7 × 10^-3</td>
<td>3825.9</td>
</tr>
<tr>
<td>UFPLA3EGL</td>
<td>0.79</td>
<td>0.72</td>
<td>83</td>
<td>1.2 × 10^-2</td>
<td>21338</td>
</tr>
<tr>
<td>UFPLA3EGS</td>
<td>1.06</td>
<td>1.00</td>
<td>290</td>
<td>3.4 × 10^-3</td>
<td>13717</td>
</tr>
</tbody>
</table>
Another key feature of adding EG nanofiller in the PLA extrusion foaming process is the barrier property of the nanoplatelets against the released gas of CFA. Because of the EG barrier property, the gas molecules must diffuse through more tortuous paths to remove from the molten bulk [1]. Thus, the gas permeability diminishes in the PLA/EG melt compounds, which assists the foaming process of the PLA melt. This effect is more pronounced for the EG particles with higher aspect ratio and better dispersion state, namely EGL and EGM, resulting in larger void fractions and cell densities.

4.3. Molecular weight changes of PLA chains over extrusion foaming in the presence of EG nanoplatelets.

Since PLA is a biodegradable polyester and does not have enough thermal stability over the melt processing, one prerequisite to study the continuous extrusion foaming of PLA-based systems is the investigation into the changes in the molecular weight and structure of PLA chains [21]. Undoubtedly, the presence of EG nanofillers profoundly impacts the chemical reactions of PLA chains during the extrusion process. The average molecular weight, molecular weight distribution and molecular structure of PLA are of great importance in the extrusion foaming. These characteristics are key parameters in controlling the rheological properties of PLA melt compounds, which assists the foaming process of the PLA melt. This effect is more pronounced for the EG particles with higher aspect ratio and better dispersion state, namely EGL and EGM, resulting in larger void fractions and cell densities.

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The degradation of PLA chains through extrusion processing mostly involves thermal chain scission and results in the formation of linear chains having lower molecular weight, branched molecules and cyclic oligomers. The acid molecules formed by the PLA chain scission act as catalysts and speed up the PLA degradation reaction more [51]. Therefore, it is required to mix an additive like a chain extender with PLA-based products to prohibit the deterioration of final structural and mechanical properties. Owing to the similarity of PLA chains with commercial synthetic polyesters such as poly(ethylene terephthalate) (PET), common PET chain extenders with epoxy functional groups have been frequently used in the PLA melt-extrusion process to keep the average molecular weight of chains in range [7, 42]. Another used additive to hinder the molecular weight reduction of PLA chains in continuous shaping processes are the thermal initiators of polymerization reactions. In several works, it has been stated that the chain extending reactions of biodegradable polymers with radical initiators in extrusion processes can substantially improve the performance of extrudate [21–23]. The involved chain extending reactions lead to the formation of linear chains with higher molecular weights and branched structures.

One group of thermal initiators of radical chain polymerization is the peroxide reagents. Benzoyl peroxide as one component of this group is applied in the present research to provide free radicals by the decomposition reaction and free macro-radicals by attacking to the PLA chains. By termination reactions of PLA macro-radicals through coupling and disproportionation reactions, longer linear chains and branched structures of PLA macromolecules can be formed. The proposed reactions of PLA chains and benzoyl peroxide initiator through melt extrusion process are schematically drawn in Fig. 7. The proposed reactions, which result in the PLA molecules with long branches or higher molecular weights, can counterbalance the effects of the PLA chain scission reaction over the extrusion process. The chain-extended structures of PLA can bring about higher melt strength and elasticity, thereby resulting in the extruded PLA foams with smaller cells, larger cell densities and higher volume expansion [52].

The molecular weight distribution of the processed virgin PLA, PLA/BP sample and PLA/BP/EGL nanocomposite obtained from GPC analysis is illustrated in Fig. 8. The determined number- and weight-average molecular weight (Mn and Mw) as well as polydispersity index (PDI) are gathered in Table 4.

As can be observed, the incorporation of BP slightly changes the molecular weight distribution of PLA chains. Nonetheless, the simultaneous presence of organic peroxide and EG nanoplatelets influences the molecular weight of PLA chains to higher extent. While Mn and Mw, and the chain populations near the peak diminishes by adding both EG and BP, a broad shoulder appears at higher molecular weights (around 10⁶ g mol⁻¹). It seems that the nanoparticles assist the organic peroxide function as a chain extender. In a similar work, it has been reported that nanoparticles beneficially affect the PLA structural changes from linear molecules to branched and star-shape structures by using a functional monomer and ester group exchange reactions in a melt process [53].

By the occurrence of chemical reactions shown in Fig. 7, PLA

![Fig. 7. Proposed chain extending reactions of PLA macromolecules induced by an organic peroxide.](Image)
macromolecules with long branches and larger molecular weight can be formed in the extrusion process. As a result, the fraction of PLA chains with higher molecular weight increases in the nanocomposite extrudate. Seemingly, the higher melt viscosity and shear viscous heat of PLA melt in the presence of EG nanoplatelet is most likely the reason of better function of BP in the nanocomposite sample. The long chain branches of the PLA macromolecules, which can create additional entanglements, can alter the rheological behavior of the melt. For instance, the long chain branches can cause the strain thickening behavior of melt in 2D extensional flow, which is of great importance in the growth stage of foaming process [40,49]. The behavior leads to higher melt strength and more resistance to the wall rupture of cells. Therefore, the foamability of PLA melt improves by such structural changes. One of the explanations for the attainment of PLA/EG foams with smaller bubbles and larger cell densities is the EG-assisted chain extension reactions of the organic peroxide and the formation of PLA macromolecules with high molecular weights (10^6 g mol^-1).

In spite of that, $M_n$ and the weight fraction of PLA molecules with molecular weights around the peak in Fig. 8 diminish in the nanocomposite sample indicating intensified chain scission reaction of PLA chains in the presence of EG nanoplatelets. Even though the chain scission and chain extending reactions of PLA macromolecules occur concurrently in the extrusion foaming process, it seems that the effects of grafting and chain extending reactions are dominant in the PLA/EG foaming process. One of the disadvantages of using organic peroxide as a chain extender for polyesters like PLA is the probability of gelation as a result of crosslinking reactions. The gel content of the obtained PLA foams was measured and the resultant data show that the gel content of all samples are in the range of 7–9 wt% with small variations. The results confirm that the presence of different types of EG nanofillers at different loadings does not noticeably influence the gelation reaction of BP, albeit the organic peroxide slightly crosslinks the PLA chains.

As mentioned before, the graphite nanoplatelets can accelerate the crystallization process of PLA after exiting die during the cooling process, at which the foaming process is concurrently progressing. Thus, the EG impacts on the PLA crystallization process are evaluated in the following subsection owing to the importance of crystallization kinetics of PLA on the foam morphology.

4.4. Quiescent and shear-induced crystallization kinetics of PLA chains in the presence of EG nanoplatelets.

The PLA crystallization from melt can change the viscoelastic properties of matrix such as shear and extensional viscosity and melt elasticity, which are critically important in the bubble nucleation and growth and corresponding foam microstructure. In the case of virgin PLA, the crystalline structures cannot dramatically improve the melt foamability due to the low crystallization rate [1,2,8]. Nanoparticles can accelerate the PLA crystallization process by providing heterogeneous nucleation sites. In this case, the need to overcome the energy barrier for the formation of primary homogeneous nuclei is reduced by the nanofiller addition [54,55]. Despite that, nanoparticles can affect the matrix crystallization process by retarding the growth stage of crystallization, which has an opposite trend in the overall crystallization kinetics comparing with the former effect.

In order to evaluate the EG effects on the crystallization process of PLA during the foaming process, the isothermal DSC experiments were carried out on UFPLA/BP and PLA/EG samples. The resultant DSC thermograms at 118 °C are illustrated in Fig. 9.

To study the effects of EG presence and particle size on the isothermal crystallization of PLA chains more precisely, Avrami model as the most widely used theory for investigating the isothermal crystallization of polymers is applied to the crystallinity degree ($X_c$) vs. time data. According to the theory, $X_c(t)$ varies with time as follows:

$$X_c(t) = 1 - \exp(-K t^n)$$

where $K$ and $n$ are overall kinetic constant and Avrami index, respectively. The Avrami parameters are determined from the slope and intercept of ln$[-\ln (1 - X_c(t))]$ vs. ln$t$ curves. The parameter $K$ shows the overall crystallization rate and the Avrami index, $n$, is related to the nucleation type and crystal growth dimension [46]. The Avrami parameters are determined for the samples and collected in Table 5.

As can be found in Fig. 9 and Table 5, the quiescent crystallization process of PLA is accelerated by the presence of ECG and EGS nanofillers. In contrast, the EG nanoplatelets with medium average size retard the isothermal crystallization of PLA. The accelerated crystallization of PLA chains in UFPLA3EGL sample that results in lower crystallization peak time, larger $K$ and smaller $n$, most likely originates from larger aspect ratio of ECG particles and better EG dispersion and delamination state in the PLA matrix. By higher interfacial area and much more accessible heterogeneous nucleation sites for the PLA crystallization, the overall crystallization rate in quiescent conditions improves in the PLA/EG nanocomposite. Comparing with UFPLA3EGL sample, the crystallization rate of PLA macromolecules in the presence of EGS particles is lower, albeit an improvement is observed in comparison with UFPLA/BP sample. In fact, it stems from smaller EGS particle size and aspect ratio that can assist the quiescent PLA crystallization rate to lower extents by

Table 4

<table>
<thead>
<tr>
<th>Sample</th>
<th>$M_n [\text{g} \text{mol}^{-1}]$</th>
<th>$M_w [\text{g} \text{mol}^{-1}]$</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Processed virgin PLA</td>
<td>$8.02 \times 10^5$</td>
<td>$105 \times 1.41$</td>
<td>1.75</td>
</tr>
<tr>
<td>UFPLA/BP</td>
<td>$7.80 \times 10^4$</td>
<td>$105 \times 1.45$</td>
<td>1.86</td>
</tr>
<tr>
<td>UFPLA3EGL</td>
<td>$7.76 \times 10^4$</td>
<td>$105 \times 2.07$</td>
<td>2.67</td>
</tr>
</tbody>
</table>
providing some heterogeneous nuclei. Contrary to them, UFPLA3EGM nanocomposite has slower crystallization kinetics comparing with UFPLA/BP sample. It seems that the retardation effect of EGM nanoplatelets on the growth stage of the PLA crystallization is dominant comparing with the influence of assisted nucleation stage. As mentioned before, the accelerated crystallization of PLA chains by EG nanofillers can greatly improve the melt strength of PLA after exiting the extrusion die.

It is noteworthy that EGL with largest particle size and aspect ratio has the most pronounced effect on the bubble nucleation stage, PLA crystallization kinetics and viscoelastic properties, though the highest void fraction and cell density is attained for another EG type, i.e. EGM. As mentioned, the crystallization kinetics of PLA chains in quiescent conditions is promoted more considerably by EGL nanoparticles owing to the good dispersion and delamination of EGL platelets. However, the PLA chains in the bulk of the foaming extrudate are not completely crystallized in the quiescent conditions. Most of them are oriented in the machine direction due to the entrance effect and pressure flow in the die, even though the chain relaxation occurs to some extent after exiting die by die swell [40,46]. Considering the chain orientation induced by the melt flow and bubble growth stage, it seems that the crystallization process of matrix proceeds in the oriented conditions [41]. Thus, the shear-induced crystallization of PLA chains in UFPLA/BP and UFPLA3EGL samples is evaluated by applying isothermal oscillatory time sweep at 135 °C after exposing the melt to a shear rate of 1 s⁻¹ for 10 s. The results are illustrated in Fig. 10. As can be seen, the storage and loss modulus gradually increase with time after showing an onset time for beginning the shear-induced crystallization of PLA. Unexpectedly, the increment of dynamic moduli for the nanocomposite commences at a longer time and keep growing at a smaller slope, indicating the lower rate of the shear-induced crystallization of PLA chains in the presence of EGM nanofiller. Despite the observed improvement in the quiescent crystallization kinetics, EGM nanoplatelets do not assist the crystallization of oriented PLA chains. In other words, the EG nanofiller does not enhance the foamability of PLA melt by accelerating the crystallization process of oriented PLA macromolecules.

Table 5
Avrami parameters and crystallization peak time (tp) determined from the isothermal DSC segment and the corresponding overall crystallinity degree determined from the subsequent DSC heating segment.

<table>
<thead>
<tr>
<th>Sample</th>
<th>tp (s)</th>
<th>K (s⁻¹)</th>
<th>n</th>
<th>Overall crystallinity degree (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>UFPLA/BP</td>
<td>1450</td>
<td>5.7 × 10⁻¹²</td>
<td>3.46</td>
<td>41.3</td>
</tr>
<tr>
<td>UFPLA3EGL</td>
<td>1096</td>
<td>9.3 × 10⁻¹²</td>
<td>2.86</td>
<td>38.8</td>
</tr>
<tr>
<td>UFPLA3EGM</td>
<td>1392</td>
<td>4.7 × 10⁻¹²</td>
<td>3.45</td>
<td>39.7</td>
</tr>
<tr>
<td>UFPLA3EGS</td>
<td>1236</td>
<td>9.5 × 10⁻¹²</td>
<td>3.14</td>
<td>39.2</td>
</tr>
</tbody>
</table>

Fig. 9. (a) Isothermal DSC curve and (b) the corresponding crystallinity degree versus time for UFPLA/BP and unfoamed PLA/EG nanocomposites at the temperature of 118 °C.

5. Concluding remarks

In this study, the PLA foaming was chemically carried out by using a continuous extrusion process. The foamability of PLA was improved by adding an organic peroxide, a CFA activator and EG nanoplatelets with different aspect ratio, size and loadings. By incorporating nanofiller
into PLA matrix, biodegradable foams having larger void contents and cell densities as well as smaller bubbles were obtained. Morphological observations confirm the heterogeneous bubble multi-nucleation function of nanofiller surfaces. Besides, the EG nanoplatelets also impact the PLA foaming process in the bubble growth stage. By the interactions of PLA chains and EG nanoplatelets, the viscoelastic properties of PLA improve. The chain extension reactions of the used organic peroxide are intensified in the presence of nanofiller, which results in an improvement in the weight-average molecular weight of PLA chains. However, more intense chain scission of the PLA chains through thermal melt-compounding and foaming process is observed for the PLA/EG nanocomposites that consequently, leads to lower number-average molecular weight of matrix. Additionally, the nanofiller solid surfaces accelerate the quiescent crystallization of PLA chains by providing heterogeneous nuclei. The beneficial influences of EG nanofiller on the extrusion foaming process of PLA improve the melt strength and elasticity, inhibit the removal of gas molecules from matrix and distribute the bubbles more uniformly in the matrix. The findings of the present work confirm that the continuous extrusion foaming of biodegradable and renewable PLA with great complexity can be improved by applying some economical additives.

Credit author statement

Seyed Mohammad Hassan Khademi: Validation, Formal analysis, Investigation, Writing - Original Draft.
Farkhonde Hemmati: Conceptualization, Methodology, Validation, Resources, Writing - Review & Editing, Visualization, Supervision, Project administration.
Mohammad Ali Aroon: Conceptualization, Resources, Writing - Review & Editing, Supervision.

References
