Superior Crystallization Kinetics Caused by the Remarkable Nucleation Effect of Graphene Oxide in Novel Ternary Biodegradable Polymer Composites

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ABSTRACT: In this study, novel ternary composites were prepared, including biodegradable poly(ethylene succinate) (PESu), poly(ethylene glycol) (PEG), and graphene oxide (GO). We have conducted a comprehensive study on whether GO can successfully promote the crystallization behaviors of PESu in the ternary composites. The results of isothermal crystallization demonstrated that with the increase of GO content in the composite (at a fixed PESu/PEG ratio), the Avrami rate constant $k$ gradually increased, indicating that the crystallization rate was faster when GO was added to the composite. The same phenomenon was also found for nonisothermal crystallization. It was found that the Mo model can adequately describe the nonisothermal crystallization behaviors of the composites. The analyses demonstrated that the $F(T)$ value estimated from the Mo model decreased when the GO content was increased. This result implied that GO promoted the nonisothermal crystallization of PESu in the ternary PESu/PEG/GO composites. Discussions on nucleation activity and microscopy observations confirmed that GO can act as a nucleation agent to further enhance the crystallization of the composites. The significant nucleation effect of GO on PESu in its novel ternary composite was first discovered in this study.

1. INTRODUCTION

The conventional plastics and polymeric materials have been explored and applied in various fields during the last few decades. However, although the conventional plastics are applicable in the industries, one of their drawbacks is that most of them are not biodegradable. Their poor biodegradability of causes a problem: waste matters of the conventional plastics lead to pollution of our environment. To resolve the pollution problem caused by the waste matters of the conventional plastics, biodegradable polymers have been developed, which can be biodegraded in the environment. Poly(ethylene succinate) (PESu) is a biodegradable polymer showing an aliphatic backbone structure. A previous literature has reported that it is a semi-crystalline polyester and can be synthesized by the condensation reaction of succinic acid and 1,2-ethanediol. In addition, PESu also shows desirable physical properties such as the processability at the molten state, resistance to chemical agents, and preferable mechanical property, leading to its potential applications in the future. Studies of PESu and its relevant systems are still progressing. The investigation on crystallization behaviors of crystalline polymers is a critical issue. Among the biodegradable polymers, PESu is a crystalline one and its behavior of crystallization should be widely discussed. The crystallization kinetics of PESu and its blends or composites have been investigated. To modify the crystallization of PESu so that the crystallization rate and kinetics of PESu can be promoted, most efforts have been made on the preparation of binary composites comprising a nucleation agent and PESu.
For example, it has been found that the carboxyl-functionalized multiwalled carbon nanotube (f-MWNT) was a nucleation agent of PESu in its binary composites.\textsuperscript{15} According to the crystallization kinetics results, the presence of f-MWNT enhanced the isothermal crystallization of PESu. Vasileiou et al.\textsuperscript{16} have also found that a SiO\textsubscript{2} particle was able to form binary composites with PESu and also increased the isothermal crystallization rate of PESu. Nonisothermal crystallization for the PESu/octavinyl-polyhedral oligomeric silsesquioxanes (PESu/ovi-POSS) composites has also been discussed by using the cooling process from the molten state.\textsuperscript{17} Relevant results demonstrated that ovi-POSS in the composites enhance the nonisothermal crystallization of PESu and the temperature of nonisothermal crystallization peak increased with the addition of ovi-POSS. As mentioned above for the binary PESu composites, including a nucleation agent in PESu may increase PESu’s crystallization rate because the nucleation agent may be able to provide more sites that can initialize the crystallization process. To gain more possibilities to further promote the crystallization of PESu, the investigation on PESu ternary composite containing a nucleation agent should also be carried out. The nucleation agent may also enhance the crystallization of PESu in the ternary composite. Furthermore, the study of PESu ternary composite can also broaden the future application of PESu.

In general, graphene and its derivatives show superior functions such as high surface area and high mechanical strength. Moreover, they can also be utilized in the preparation of biomaterials. For the application of graphene, avoiding its aggregation is always a critical issue. Graphene oxide (GO) is one of the attractive graphene derivatives. By the formation of GO, the extent of aggregation during the application process can be decreased. The most used method in the fabrication of GO is the Hummer’s method.\textsuperscript{18} According to the Hummer’s method,\textsuperscript{18} general graphite can be oxidized to form GO by mixing with sulfuric acid, sodium carbonate, and potassium permanganate. GO has also been used to prepare biodegradable polymer composites\textsuperscript{19–22} such as the composites of poly(ethylene adipate)/GO, poly(butylen succinate-co-adipate)/GO, poly(l-lactide)/GO, and poly(\textepsilon-caprolactone)/

Figure 1. Isothermal crystallization thermograms of neat PESu and the PESu/PEG/GO = 93/7/x composites at (a) $T_\text{c} = 50$ °C, (b) $T_\text{c} = 52$ °C, (c) $T_\text{c} = 54$ °C, and (d) $T_\text{c} = 56$ °C. The x values are the relative weight ratios of GO in the composites and are 0, 0.5, 1, and 2.
GO. In the biodegradable polymer composites, one of the functions of GO was that it acted as the nucleation agent of the semicrystalline biodegradable polymers so that polymers' crystallization behaviors were altered and modified. The modification between GO and the polymer can be used to improve the properties of polymeric composites. 23,24 A comparative study for the PESu composites with the addition of various fillers such as the multiwalled carbon nanotube, silver nanoparticle, GO, and org-GO has also been reported.25 Plasticizers can modify the properties of polymers. For example, the crystallization behaviors of polymers can be promoted by plasticizers. Adding a nucleation agent in a crystalline polymer accompanied by a plasticizer may further enhance the crystallization behaviors of the crystalline polymer. Although PESu is a biodegradable material that has attracted much attention, the influence of the synergistic effect of plasticization and nucleation on the crystallization of PESu has not been clearly elucidated in the literature. In this work, for the first time, the biodegradable PESu was mixed with a plasticizer like polymer, poly(ethylene glycol) (PEG), and a nucleation agent like graphene derivative, GO. The crystallization rate of PESu was expected to be significantly increased by the presence of PEG and GO. We found that GO could obviously influence the crystallization rate of PESu and further promote the crystallization kinetics of PESu in the ternary PESu/PEG/GO composites. Because the nucleation effect of GO can effectively increase the crystallization rate and related physical properties, the PESu/PEG/GO ternary composites prepared in this study are expected to exhibit shorter processing time and cycle, as well as desirable dimension stability and mechanical properties. In addition, the ternary composites containing GO in this study can be expected to be developed as heat-resistant and conductive materials in the future. We focused on clarifying the influence of GO on the crystallization kinetics of PESu in the ternary PESu/PEG/GO composites in this work.

2. RESULTS AND DISCUSSIONS

2.1. Studies of Thermal Behaviors. General differential scanning calorimetry (DSC) thermal scans were preliminarily...
carried out to detect the thermal properties of neat PESu, binary PESu/PEG blends, binary PESu/GO composites, and ternary PESu/PEG/GO composites. The data of the PESu/PEG = 93/7 blend, PESu/GO = 93/2 composite, and PESu/PEG/GO = 93/7/2 composite were selected as the typical results for the demonstration. Relevant results are shown in Figure S1 in the Supporting Information. It should be noted that in Figure S1, based on the ternary composition of PESu/PEG/GO, neat PESu is coded as 100/0/0, and PESu/PEG = 93/7 blend and PESu/GO = 93/2 composites are coded as 93/7/0 and 93/0/2, respectively. The $T_c$ decreased with the addition of PEG, suggesting the plasticizer effect in the presence of PEG. In addition, the cold crystallization temperatures ($T_c$) in binary PESu/PEG blend and binary PESu/GO composite were all lower than those of the neat PESu, indicating that PEG and GO can promote the crystallization of PESu. It should be noted that PEG may also somewhat suppress the aggregation of GO to make GO more effective in promoting the cold crystallization of PESu in the ternary composite. The ternary PESu/PEG/GO composite revealed a preferable crystallization behavior in the presence of PEG and GO. To understand the influence of GO on the crystallization behaviors in the ternary PESu/PEG/GO composites, the studies of isothermal and nonisothermal crystallization kinetics have been also carried. Relevant results about the crystallization kinetics are shown in the following sections.

2.2. Isothermal Crystallization Kinetics of Ternary PESu/PEG/GO Composites. The studies of isothermal crystallization for ternary PESu/PEG/GO composites were performed. Figure 1 displays the isothermal crystallization thermograms for neat PESu and the PESu/PEG/GO = 93/7/x composites at different $T_c$: (a) $T_c = 50 \degree C$, (b) $T_c = 52 \degree C$, (c) $T_c = 54 \degree C$, and (d) $T_c = 56 \degree C$. The values of $x$ are 0, 0.5, 1, and 2, and they imply the relative weight ratios of GO in the ternary composites. As the results demonstrated by Figure 1a–d show, by gradually increasing the GO content in the composites, the isothermal crystallization peak shifted significantly to a shorter time regardless of the change in $T_c$. That is, GO showed an apparent influence on the isothermal crystallization of the ternary composites. Similar results were also found in the PESu/PEG/GO composites with different compositional series, as shown in Figures S2–S4 in the Supporting Information. The addition of GO can further accelerate the isothermal crystallization of PESu in the ternary PESu/PEG/GO composites. Relevant studies of the isothermal crystallization were also performed. The Avrami equation$^{26,27}$ was used to analyze the isothermal kinetics of the ternary PESu/PEG/GO composites. The logarithmic form of the Avrami equation is shown in the following equation

$$\log[-\ln(1 - X_t)] = \log k + n \log t$$

In the equation, $X_t$ shows the relative degree of crystallinity at time $t$. The Avrami exponent $n$ is associated with the crystallization mechanism, and the rate constant $k$ can be correlated to the crystallization rate of isothermal crystallization. The results of some representative ternary composites processed by the Avrami equation are shown in Figure 2. Figure 2 displays the plots of the logarithmic Avrami equation for various PESu/PEG/GO composites: (a) PESu/PEG/GO = 99/1/2, (b) PESu/PEG/GO = 97/3/2, (c) PESu/PEG/GO = 95/5/2, and (d) PESu/PEG/GO = 93/7/2. A linear relationship was found according to the fitting results of Figure 2. That is, the Avrami model can properly describe the isothermal crystallization kinetics of the ternary PESu/PEG/GO composites. It should be noted that the Avrami model can also describe the isothermal crystallization kinetics of the neat PESu and the relevant PESu/PEG binary blends. The fitting results of their logarithmic plots are summarized in the Figure S5 in the Supporting Information.

According to the fitting results, we also estimated the values of Avrami exponent $n$ and rate constant $k$ for the composites. Table 1 shows the relevant kinetic parameters calculated by the fitting results for neat PESu and the PESu/PEG/GO = 93/7/x composites ($x = 0, 0.5, 1,$ and 2). The values of crystallization half-time ($t_{0.5}$) estimated by the $n$ and $k$ are also tabulated in the tables. The $t_{0.5}$ can be determined by the following formula

$$t_{0.5} = \left(\frac{\ln 2}{k}\right)^{1/n}$$

Generally, $1/t_{0.5}$ can be associated with the crystallization rate of the composites. In Table 1 for the kinetic parameters of the PESu/PEG/GO = 93/7/x composites, it is found that $1/t_{0.5}$ increased with the increase in the GO content in the composites, inferring the promotion of the isothermal kinetics with the incorporation of GO in the composites. In the meantime, larger $k$ values were obtained by adding GO in the composites. Similar results are also presented in Tables S1–S3 in the Supporting Information for the PESu/PEG/GO composites with different compositional series. It is clear that the $k$ value systematically increased with the increase in the GO content in the ternary composites. The tendency of $k$ is also shown in Figure 3 for each compositional series of the ternary PESu/PEG/GO composites. Both of the results of $1/t_{0.5}$ and $k$ might be attributed to the nucleation effect of GO in

| PESu/PEG/GO (relative weight ratio) | $T_c$ (°C) | $n$ | $k$ (min$^{-1}$) | $t_{0.5}$ (min) | $1/t_{0.5}$ (min$^{-1}$) |
|------------------------------------|----------|----|----------------|----------------|-------------------------|
| 100/0/0                            | 50       | 2.52 | 0.0051         | 7.012          | 0.143                   |
| 52                                 | 2.55     | 0.0039 | 7.683          | 0.130          |
| 54                                 | 2.38     | 0.0038 | 8.953          | 0.112          |
| 56                                 | 2.49     | 0.0023 | 9.905          | 0.101          |
| 50                                 | 2.55     | 0.0389 | 3.053          | 0.328          |
| 52                                 | 2.39     | 0.0252 | 3.996          | 0.250          |
| 54                                 | 2.14     | 0.0227 | 4.925          | 0.203          |
| 56                                 | 2.03     | 0.0192 | 5.823          | 0.172          |
| 93/7/0                            | 50       | 2.68  | 0.1901         | 1.621          | 0.617                   |
| 52                                 | 2.70     | 0.1711 | 1.934          | 0.517          |
| 54                                 | 2.65     | 0.0735 | 2.331          | 0.429          |
| 56                                 | 2.62     | 0.0441 | 2.858          | 0.350          |
| 93/7/1                            | 50       | 2.43  | 0.4281         | 1.219          | 0.820                   |
| 52                                 | 2.42     | 0.2634 | 1.492          | 0.670          |
| 54                                 | 2.40     | 0.1659 | 1.817          | 0.550          |
| 56                                 | 2.40     | 0.0922 | 2.317          | 0.432          |
| 93/7/2                            | 50       | 2.53  | 0.7572         | 0.966          | 1.036                   |
| 52                                 | 2.53     | 0.4978 | 1.140          | 0.877          |
| 54                                 | 2.52     | 0.3212 | 1.358          | 0.737          |
| 56                                 | 2.51     | 0.2022 | 1.635          | 0.612          |

The $x$ values are the relative weight ratios of GO in the composites and are 0, 0.5, 1, and 2.
the ternary composites. GO exhibited the same effect of nucleation in the ternary PESu/PEG/GO composites with various compositions. The $n$ values relating to the crystallization mechanism were also analyzed. We found that the $n$ value did not change significantly with the addition of GO in the composites. The addition of GO would not significantly influence the crystallization mechanism of the composites. The addition of GO mainly promoted the isothermal crystallization rate of the PESu in the PESu/PEG/GO composites.

2.3. Nonisothermal Crystallization Kinetics of Ternary PESu/PEG/GO Composites. We also discussed the nonisothermal crystallization behaviors and kinetics for the PESu/PEG/GO ternary composites. The experiments of nonisothermal crystallization were carried out by first melting the specimens above the melting temperature and then cooling them at the rates of 4, 6, 8, and 10 °C/min. Relevant cooling curves related to the nonisothermal crystallization were recorded. Typical results are shown in Figure 4. Figure 4 demonstrates the nonisothermal thermograms of neat PESu and the PESu/PEG/GO = 93/7/x composites. Two features were found by the results. First, the intensity of the nonisothermal crystallization peak was gradually enhanced with the increase in the GO content. Second, the nonisothermal crystallization peak shifted toward higher temperature with the addition of GO in the ternary composites. The enhanced intensity of the nonisothermal crystallization peak is due to the promoted nonisothermal crystallization of PESu caused by the increase of the GO content. On the other hand, the GO acted as an efficient nucleation agent so that the ternary composites crystallized earlier at a higher temperature during the nonisothermal cooling process. Similar results were also found in the composites with different compositional series shown in Figures S6–S8. The results of the nonisothermal crystallization process are comparable to those of the isothermal crystallization process. The presence of GO will also obviously enhance the nonisothermal crystallization behavior of PESu in the ternary composites.

The experimental data of the nonisothermal crystallization were also analyzed by using the mathematic models such as the Avrami equation, the Ozawa equation, and the Mo model. We found that the Avrami equation and the Ozawa equation cannot properly describe the nonisothermal crystallization behaviors of the PESu/PEG/GO composites, owing to the nonlinear characteristic by fitting the experimental data to the theoretical estimations. For brevity, relevant results of the Avrami and the Ozawa analyses are not shown here. Mo and coworkers have derived a model to study the nonisothermal crystallization. The Mo model shows the correlation between the cooling rate and crystallization time. The related equation is given below

$$\log \Phi = -a \log t + \log F(T)$$
In the equation, Φ is the cooling rate and t is the crystallization time of nonisothermal crystallization. It should be noted that t can be converted by the crystallization temperature (T) and the cooling rate using the formula \( t = T_0 - T/Φ \). \( F(T) \) can be related to the value of the cooling rate required to reach a defined degree of crystallinity at a certain temperature in the unit crystallization time. The Mo index "a" is the ratio between the Avrami exponent \( (n) \) and the Ozawa exponent \( (m) \). The Mo model fitting results of neat PESu and the relevant PESu/PEG binary blends are shown in Figure 5. Similar to the results for neat PESu, we also found that the fitting results of the PESu/PEG/GO composites displayed a linear relationship. Figure 6 shows the Mo model fitting results for some representative ternary PESu/PEG/GO composites.

The nonisothermal crystallization parameters can be calculated by the fitting results of the Mo model. In general, the \( F(T) \) value of the Mo model can be correlated with the rate of nonisothermal crystallization.\(^{31,32} \) A smaller \( F(T) \) value indicates a faster rate of nonisothermal crystallization. By the fitting results, we found that as the GO content in the composite increased, the \( F(T) \) values became smaller. On the other hand, there was no significant change in the a value obtained from the fitted results. Typical results for the parameters calculated by the Mo model are summarized in Table 2 for the PESu/PEG/GO = 93/7/\( x \) composites. The results of the PESu/PEG/GO composites with different compositional series are also demonstrated in Tables S4–S6 in the Supporting Information. The addition of GO promoted the nonisothermal crystallization rate of the ternary PESu/PEG/GO composites by the nucleation effect. The tendency that the \( F(T) \) value decreases as the GO content increases in the PESu/PEG/GO composites is also illustrated in Figure 7.

2.4. Scanning Electron Microscopy Images of PESu/PEG/GO Ternary Composites. Scanning electron microscopy (SEM) was used to observe the morphology and detect the dispersion of GO in the ternary composites. The typical results of the PESu/PEG/GO = 93/7/\( x \) composite are demonstrated in Figure 8. Magnifications of 2000× and 6000× were used in SEM observation. The morphology in Figure 8 shows that GO can be properly dispersed in the

Figure 4. DSC nonisothermal crystallization results of neat PESu and the PESu/PEG/GO = 93/7/\( x \) composites with different cooling rates: (a) 4, (b) 6, (c) 8, and (d) 10 °C/min. The \( x \) values are the relative weight ratios of GO in the composites and are 0, 0.5, 1, and 2.
composite matrix, which means that the aggregation of GO in the composite is not obvious. The lateral size of GO sheet is about 2−4 μm. The GO sheets dispersed in the composite have a lateral dimension of about 2−4 μm. In addition, the thickness of the GO sheets is close to the scale of around few nanometers. This similar GO morphology has also been resolved in the literature in the polymer/GO composite system. The presence of GO in PESu/PEG/GO composite can be confirmed.

2.5. Spherulite Morphologies and Nucleation Density of PESu/PEG/GO Ternary Composites by Adding GO.

Spherulite morphologies of the ternary PESu/PEG/GO composites were observed by using polarized optical microscopy (POM). In addition, the nucleation density was also explored. The graphs of the PESu/PEG/GO = 93/7/x samples are selected as the typical results to demonstrate the spherulite morphologies. Figure 9 reveals the POM graphs of (a) neat PESu, (b) PESu/PEG = 99/1 blend, (c) PESu/PEG = 97/3 blend, (d) PESu/PEG = 95/5 blend, and (e) PESu/PEG = 93/7 blend.

2.6. Wide Angle X-ray Diffraction Studies for PESu/PEG/GO Ternary Composites.

WAXD studies for the ternary PESu/PEG/GO composites were also performed. All of the polymeric samples subjected to WAXD measurements were crystallized at 50 °C. Figure 10 demonstrates the WAXD results for the specimens of neat PESu, neat GO, PESu/PEG/GO = 93/7/0, and PESu/PEG/GO = 93/7/2. For neat PESu, WAXD results showed three peaks at 20.7, 22.9, and 23.5°, which can be resulted from the diffraction planes of (021), (121), and (200), respectively. On the other hand, neat GO displayed a characteristic peak at about 11°. This characteristic peak can be related to the (110) diffraction plane of GO. We further found that in the PESu/PEG/GO ternary composites, this diffraction peak disappeared. This finding means that GO can be effectively dispersed and exfoliated in the composite matrix. A similar result has also been reported in the literature. In addition, it also revealed that the diffraction patterns of PESu/PEG/GO = 93/7/0 and PESu/PEG/GO = 93/7/2 were almost the same as those of neat PESu. This phenomenon implies that the additives as PEG and GO would not change the crystal structures of PESu under crystallization. Moreover, it can also correlate the abovementioned WAXD
results with the insignificant change on the $n$ values estimated by the Avrami equation.

2.7. Effect on Nucleation Activity of Nonisothermal Crystallization by Adding GO in Ternary Composites.

We also discussed the nucleation effect of GO during nonisothermal crystallization in this work. The nucleation activity of the nonisothermal crystallization was investigated. The value of nucleation activity can be used to evaluate the nucleation ability for a specific nucleation agent. The nucleation activity ($\Phi$) has been proposed by Dobreva and Gutzow.\textsuperscript{34,35} using the following formula

$$\Phi = \frac{B^*}{B}$$

The values of $B$ and $B^*$ can be associated with the homogeneous and heterogeneous nucleation, respectively. It could associate $B$ with the nonisothermal crystallization behaviors of a neat polymer and $B^*$ with the nonisothermal crystallization behaviors of the polymer composite containing a nucleation agent. For the neat polymer, $\Phi$ is equal to 1, but for the polymer composite, the $\Phi$ value decreases (less than 1) after the addition of nucleation agent usually suggests the significant nucleation activity caused by the nucleation agent.\textsuperscript{34,35} For the $B$ value, it can be estimated by the following formula for a neat polymer

$$\ln \beta = \text{Const} - \frac{B}{\Delta T_p^2}$$

It should be noted that $\beta$ is the cooling rate of nonisothermal crystallization and $\Delta T_p$ is $T_m - T_c$. Moreover, the formula shown below can be used to acquire the $B^*$ value for the polymer composite with a nucleation agent.

$$\ln \beta = \text{Const} - \frac{B^*}{\Delta T_p^2}$$

Figure 6. Mo model plots of log$\Phi$–vs–log$t$ for the nonisothermal crystallization of the ternary PESu/PEG/GO composites. The ternary compositions are (a) 99/1/2, (b) 97/3/2, (c) 95/5/2, and (d) 93/7/2.
Table 2. Nonisothermal Crystallization Parameters Calculated for the PESu/PEG/GO = 93/7/x Composites

| PESu/PEG/GO (relative weight ratio) | \(x_i\) (%) | \(a\) | \(F(T)\) |
|------------------------------------|-------------|------|--------|
| 100/0/0                            |             |      |        |
| 20                                 | 1.09        | 20.18|        |
| 40                                 | 1.13        | 28.17|        |
| 60                                 | 1.16        | 35.88|        |
| 80                                 | 1.17        | 43.93|        |
| 93/7/0                             |             |      |        |
| 20                                 | 1.04        | 16.59|        |
| 40                                 | 1.08        | 23.01|        |
| 60                                 | 1.09        | 28.78|        |
| 80                                 | 1.11        | 35.57|        |
| 93/7/0.5                           |             |      |        |
| 20                                 | 1.08        | 12.54|        |
| 40                                 | 1.16        | 17.46|        |
| 60                                 | 1.23        | 22.94|        |
| 80                                 | 1.32        | 30.96|        |
| 93/7/1                             |             |      |        |
| 20                                 | 1.17        | 9.722|        |
| 40                                 | 1.25        | 14.2 |        |
| 60                                 | 1.33        | 19.18|        |
| 80                                 | 1.41        | 26.47|        |
| 93/7/2                             |             |      |        |
| 20                                 | 1.15        | 7.093|        |
| 40                                 | 1.23        | 10.06|        |
| 60                                 | 1.27        | 12.91|        |
| 80                                 | 1.32        | 16.63|        |

*The \(x\) values are the relative weight ratios of GO in the composites and are 0, 0.5, 1, and 2.

By the slopes of \(\ln(i/\text{vs}−1/\Delta T)\) plots, the \(B\) and \(B^*\) values of a neat polymer and the composite can be obtained. Typical results from neat PESu and the ternary composites of PESu/PEG/GO = 93/7/0.5, PESu/PEG/GO = 93/7/1, and PESu/PEG/GO = 93/7/2 are demonstrated in Figure 11. We further estimated the slopes in the plots of Figure 11 to obtain the \(\phi\) values. In general, a smaller \(\phi\) value means a more pronounced heterogeneous nucleation in the composites. We found that the \(\phi\) values of the composites in the presence of GO were all smaller than those of the neat PESu, indicating a significant heterogeneous nucleation caused by GO in the composites. GO was found to be a useful nucleation agent displaying significant nucleation activity in the ternary PESu/PEG/GO composites during the nonisothermal crystallization. In addition, we also found that the \(\phi\) value decreased with increasing the GO content in the composite. The tendency between \(\phi\) and GO content in the PESu/PEG/GO = 93/7/x composites is illustrated in Figure 12. It should be noted that the \(\phi\) value of neat PESu (\(\phi = 1\), with a GO content of 0) is also shown in Figure 12 for comparison. We found that in the same composition series as PESu/PEG/GO = 93/7/x, when the GO content in the ternary composites increased, the \(\phi\) value decreased, proving the significant nucleation activity of GO in the ternary PESu/PEG/GO composites. Similar studies on nucleation activity have also been performed in the literature\(^{36-38}\) to discuss the influence of a nucleation agent on the crystallization behaviors of polymer composite systems. Both the results from POM and nucleation activity indicated that GO is an effective nucleation agent and can further promote the crystallization kinetics of the ternary PESu/PEG/GO composites.

2.8. Investigations on Effective Activation Energy

The investigations on the effective activation energy were also performed for the nonisothermal crystallization of the composites. The isosconversion method reported by Fried-

\(^{39,40}\) was applied for estimating the effective activation energies of the composites. The details about the Friedman method are described in the Supporting Information. Figures 13 and 14 demonstrate the important results about the Friedman estimation of the effective activation energy. In Figure 13, the plots of \(\ln(dX/dT)\) versus \(1/T\) for neat PESu, PESu/PEG/GO = 93/7/0, and PESu/PEG/GO = 93/7/2 composites are displayed. Furthermore, the effective energy values of neat PESu, PESu/PEG/GO = 93/7/0, and PESu/PEG/GO = 93/7/2 composites are illustrated in Figure 14. The estimations of the Friedman method indicated that the effective activation energy values of neat PESu were different from those of the composites. First, we discovered that the composite of PESu/PEG/GO = 93/7/0 presented the smaller values of effective activation energy. This might be attributed to the higher chain mobility for crystallization caused by the plasticizer effect of PEG in the composite. Second, it was demonstrated that adding GO in the ternary composites would not lead to a significant drop in the effective activation energy. By this phenomenon, it could be deduced that GO would not increase the chain mobility of PESu as a plasticizer so that the activation energy was not further decreased with the addition of GO in the ternary composites. It should be noted that GO mainly acted as a nucleation agent to nucleate PESu for its crystallization. In the ternary composites, GO might come in contact with some chain segments of PESu, and PESu’s chain transportation was able to be influenced to a certain extent by GO.

3. CONCLUSIONS

In this work, ternary PESu/PEG/GO composites were prepared and investigated. The effect of GO on isothermal and nonisothermal crystallization kinetics of ternary PESu/PEG/GO composites was mainly discussed. We found that the addition of GO to the ternary composites can cause a significant nucleation effect and further promote the crystallization kinetics of the ternary composites. The results of the isothermal crystallization indicated that increasing the GO content in the ternary composite will gradually increase the Avrami rate constant \(k\), which means that increasing the GO content in the composite increased the crystallization rate. A similar phenomenon was also discovered for the nonisothermal crystallization behaviors of the composites. The results showed that when the GO content in the composite increased, the \(F(T)\) value estimated by the Mo method decreased. The presence of GO was able to enhance the nonisothermal crystallization rate of the ternary PESu/PEG/GO composites. GO can introduce significant nucleation in the composites so that the addition of GO can increase the isothermal and nonisothermal crystallization rates. POM micrographs showed that when GO was incorporated into the ternary composites, the spherulite density increased significantly. Moreover, the pronounced nucleation effect caused by GO was confirmed by the analysis results of nucleation activity. Both the findings from POM and nucleation activity revealed that GO is an effective nucleation agent in ternary PESu/PEG/GO composites and can further promote the crystallization kinetics of the composites. In the study of the effective activation energy, it was concluded that GO mainly acted as a nucleation agent rather than as a plasticizer to significantly reduce the effective activation energy of the composites. The results of this study clearly demonstrated that the nucleation effect of GO can obviously
promote the crystallization rate and kinetics of the ternary PESu/PEG/GO composites. GO is an effective nucleation agent for nucleating PESu to enhance its crystallization in the ternary composites.

4. EXPERIMENTAL SECTION

4.1. Materials. The poly(ethylene succinate) (PESu) used in this study was purchased from Scientific Polymer Products (SP2). It has a $T_g$ of $-14$ °C and a $T_m$ of 103 °C. The molecular weight of PESu was 10,000 g/mol according to the data from the manufacturer. The poly(ethylene glycol) (PEG) used in this study was provided by Sigma-Aldrich. $T_g$, $T_m$, and molecular weight of PEG are $-60$ °C, 56 °C, and 2000 g/mol, respectively. A commercial GO was purchased from Euflex Technology Corp. (Taipei, Taiwan).

4.2. Preparation of Composites. The composites of PESu/PEG/GO were prepared by the solution-blending method with the solvent of dimethylformamide (DMF). The preparation of the PESu/PEG/GO = 93/7/2 composite is shown here to demonstrate the general preparation of the ternary composites. To obtain the composite solution, PESu and PEG were predissolved in DMF together (PESu $\sim 0.465$ g, PEG $\sim 0.035$ g, and DMF $\sim 8$ mL). On the other hand, GO was separately dispersed in DMF and the ultrasonication treatment was adopted to enhance the dispersion of GO in DMF (GO $\sim 0.01$ g and DMF $\sim 8$ mL). The solutions of PESu/PEG and GO were then mixed together to get the ternary PESu/PEG/GO solution. The PESu/PEG/GO solution was then cast onto either glass of the aluminum substrates at 60 °C for 24 h. The as-cast films were further dried in a vacuum oven at 60 °C for 5 days, so that the residual solvent could be removed before measurements. The PESu/PEG/GO composites with different ternary compositions were also prepared in the same way as the PESu/PEG/GO = 93/7/2 composite.

4.3. Characterization. DSC experiments were performed using a DSC-8500 (PerkinElmer, Waltham, MA, USA) equipped with a mechanical intracooler under a nitrogen atmosphere. The thermal behaviors of the composites were

![Figure 7. Plots demonstrating the tendency of $F(T)$ relative to GO content in each compositional series of the ternary PESu/PEG/GO composites: (a) PESu/PEG/GO = 99/1/x, (b) PESu/PEG/GO = 97/3/x, (c) PESu/PEG/GO = 95/5/x, and (d) PESu/PEG/GO = 93/7/x. The x value is the GO content (in relative weight ratio) in the composite.](https://dx.doi.org/10.1021/acsomega.0c04658)

![Figure 8. SEM images of the PESu/PEG/GO = 93/7/2 composite. Magnifications of the images are 2000x and 6000x.](https://dx.doi.org/10.1021/acsomega.0c04658)
measured using a heating rate of 20 °C/min. $T_g$ values were taken as the onset of transition. The specimens for studying the isothermal crystallization were first melted above the melting point of PESu (130 °C) and then quenched to their crystallization temperatures ($T_c$) to crystallize isothermally. To investigate the nonisothermal crystallization, samples were treated by a melting−cooling process. The samples were premelted at the temperature higher than the melting point of PESu and then cooled at the cooling rates from 4 to 10 °C/min. The exothermic curves of cooling were recorded to analyze the nonisothermal crystallization behavior of the composites.

A polarizing microscope (Olympus CX41, Olympus, Tokyo, Japan) was used to observe the spherulite and nucleation morphology of the composites. A Linkam THMS-600 microscopic hot stage was utilized to control the temperature of the specimens. The samples for the spherulite and nucleation observation were first melted and then quickly

Figure 9. POM graphs of (a) neat PESu, (b) PESu/PEG/GO = 93/7/0, (c) PESu/PEG/GO = 93/7/0.5, (d) PESu/PEG/GO = 93/7/1, and (e) PESu/PEG/GO = 93/7/2 after crystallization at 50 °C.

Figure 10. Results of WAXD for the neat PESu, neat GO, PESu/PEG/GO = 93/7/0 composite, and PESu/PEG/GO = 93/7/2 composite. The polymeric samples for WAXD study were isothermally crystallized at 50 °C.

Figure 11. $\ln(\beta) - \frac{1}{\Delta T_p^2}$ plots of neat PESu and the ternary composites of PESu/PEG/GO = 93/7/0.5, PESu/PEG/GO = 93/7/1, and PESu/PEG/GO = 93/7/2.

Figure 12. Plot displaying the tendency of $\phi$ relative to GO content in the PESu/PEG/GO = 93/7/x composites. The x value is the GO content (in relative weight ratio) in the composite.
moved to the hot stage controlled at the desired crystallization temperatures ($T_c$).

SEM (Hitachi S3000) was carried out to resolve the phase morphology. Blend films for morphological observation were solution-casted to be thick enough in order to conveniently examine the fracture surface of the cross section. Before SEM observation, the fractured blend samples were coated with gold by vapor deposition using vacuum sputtering.

A wide-angle X-ray diffraction (WAXD) instrument, Bruker D2 PHASER (Bruker, Billerica, MA, USA), was utilized to investigate the crystalline structures of neat PESu and its composites. The WAXD instrument is used with copper $\text{k}_\alpha$ radiation ($30 \text{ kV}$ and $10 \text{ mA}$). We performed all scans for the samples under scanning $2\theta$ angles between 5 and 50° with a speed of 1 °/min.

Figure 13. Plots of $\ln(dX/dT)$ vs $1/T_x$ for (a) neat PESu, (b) PESu/PEG/GO = 93/7/0, and (c) PESu/PEG/GO = 93/7/2 composites.

Figure 14. Effective activation energy values of neat PESu, PESu/PEG/GO = 93/7/0, and PESu/PEG/GO = 93/7/2 composites.

### ASSOCIATED CONTENT

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c04658.
Friedman method to study the effective activation energy, isothermal crystallization parameters and thermograms of different compositions, nonisothermal crystallization parameters and thermograms of different compositions, DSC thermal scans ( neat PESu, binary PESu/PEG = 93/7 blend, binary PESu/GO = 93/2 composite, and ternary PESu/PEG/GO = 93/7/2 composite), and EDX results for the PESu/PEG/GO = 93/7/2 composite

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**Notes**

The authors declare no competing financial interest.

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**REFERENCES**

(1) Chen, J.-K.; Hsieh, C.-Y.; Huang, C.-F.; Li, P.-m. Characterization of patterned poly(methyl methacrylate) brushes under various structures upon solvent immersion. J. Colloid Interface Sci. 2009, 338, 428–434.

(2) Chen, H.-P.; Nagarajan, S.; Woo, E. M. Unusual Radiating-Stripe Morphology in Nonequimolar Mixtures of Poly(L-lactic acid) with Poly(D-lactic acid). Macromolecules 2020, 53, 2157–2168.

(3) Domes, S.; Filiz, V.; Nitsche, J.; Frömsdorf, A.; Förster, S. Covalent attachment of polymersomes to surfaces. Langmuir 2010, 26, 6927–6931.

(4) Yeh, Y.-T.; Woo, E. M. Anatomy into interior lamellar assembly in nuclei-dependent diversified morphologies of poly(L-lactic acid). Macromolecules 2018, 51, 7722–7733.

(5) Parra, D. F.; Fasaro, J.; Gaborido, F.; Rosa, D. S. Influence of poly(ethylene glycol) on the thermal, mechanical, morphological, physical—chemical and biodegradation properties of poly(3-hydroxybutyrate). Polym. Degrad. Stab. 2006, 91, 1954–1959.

(6) Li, Y.-D.; Fu, Q.-Q.; Wang, M.; Zeng, J.-B. Morphology, crystallization and rheological behavior in poly(ethylene succinate)/cellulose nanocrystal nanocomposites fabricated by solution coagulation. Carbohydr. Polym. 2017, 164, 75–82.

(7) Yang, J.; Pan, P.; Hua, L.; Xie, Y.; Dong, T.; Zhu, B.; Inoue, Y.; Feng, X. Fractionated crystallization, polymorphic crystalline structure, and spherulite morphology of poly(ethylene adipate) in its miscible blend with poly(ethylene succinate). Polymer 2011, 52, 3460–3468.

(8) He, X.; Qiu, Z. Effect of poly(ethylene adipate) with different molecular weights on the crystallization behavior and mechanical properties of biodegradable poly(L-lactide). Thermochim. Acta 2018, 659, 89–95.

(9) Woo, E. M.; Yen, K.-C.; Yeh, Y.-T.; Wang, L.-Y. Biometrically structured lamellae assembly in periodic banding of poly(ethylene adipate) crystals. Macromolecules 2018, 51, 3845–3854.

(10) Tsui, A.; Frank, C. W. Comparison of anhydrous and monohydrated forms of orotic acid as crystal nucleating agents for poly(3-hydroxybutyrate-co-3-hydroxyvalerate). Polymer 2014, 55, 6364–6372.

(11) El-Mahdy, A. F. M.; Liu, T.; Kuo, S.-W. Direct synthesis of nitrogen-doped mesoporous carbons from triazine-functionalized resol for CO2 uptake and highly efficient removal of dyes. J. Hazard. Mater. 2020, 391, 121163.

(12) Ishii, M.; Okazaki, M.; Shibusaki, Y.; Ueda, M.; Teranishi, T. Convenient synthesis of aliphatic polypesters by distannoxane-catalyzed polycondensation. Biomacromolecules 2001, 2, 1267–1270.

(13) Qiu, Z.; Ikehara, T.; Nishi, T. Crystallization behaviour of biodegradable poly(ethylene succinate) from the amorphous state. Polymer 2003, 44, 5429–5437.

(14) Qiu, Z.; Fujimura, S.; Komura, M.; Nakajima, K.; Ikehara, T.; Nishi, T. Nonisothermal crystallization kinetics of poly(ethylene succinate) and poly(ethylene adipate). Polym. J. 2004, 36, 642–646.

(15) Zhu, S.; Zhao, Y.; Qiu, Z. Crystallization kinetics and morphology studies of biodegradable poly(ethylene succinate)/multi-walled carbon nanotubes nanocomposites. Thermochim. Acta 2011, 517, 74–80.

(16) Vasilievou, A. A.; Papageorgiou, G. Z.; Kontopoulos, M.; Docoslis, A.; Bikisaris, D. Covalently bonded poly(ethylene succinate)/SiO2 nanocomposites prepared by in situ polymerization. Polymer 2013, 54, 1018–1032.

(17) Tang, L.; Qiu, Z. Crystallization kinetics and morphology of biodegradable poly(ethylene propionate)/octavinyl-polyhedral oligomeric silsesquioxanes nanocomposites. Ind. Eng. Chem. Res. 2014, 53, 11365–11370.

(18) Hummers, W. S., Jr.; Offeman, R. E. Preparation of graphitic oxide. J. Am. Chem. Soc. 1958, 80, 1339.

(19) Jiang, Z.; Qiu, Z. Unusual crystallization behavior of biodegradable poly(ethylene adipate) based nanocomposites induced by graphene oxide. RSC Adv. 2015, 5, 55486–55491.

(20) Zhou, W.; Wang, X.; Wang, P.; Zhang, W.; Ji, J. Enhanced mechanical and thermal properties of biodegradable poly(butylene succinate-co-adipate)/graphene oxide nanocomposites via in situ polymerization. J. Appl. Polym. Sci. 2013, 130, 4075–4080.

(21) Chen, H.-m.; Zhang, W.-b.; Du, X.-c.; Yang, J.-h.; Zhang, N.; Huang, T.; Wang, Y. Crystallization kinetics and melting behaviors of poly(l-lactide)/graphene oxides composites. Thermochim. Acta 2013, 566, 57–70.

(22) Hua, L.; Kai, W. H.; Inoue, Y. Crystallization behavior of poly(ε-caprolactone)/graphite oxide composites. J. Appl. Polym. Sci. 2007, 106, 4225–4232.

(23) Dhayal, V.; Hashmi, S. Z.; Kumar, U.; Choudhary, B. L.; Kuznetsov, A. E.; Dala, S.; Kumar, S.; Saya, S.; Doliá, S. N.; Alvi, P. A. Spectroscopic studies, molecular structure optimization, and investigation of structural and electrical properties of novel and biodegradable Chitosan-GO polymer nanocomposites. J. Mater. Sci. 2020, 55, 14829–14847.

(24) Khichar, K. K.; Dangi, S. B.; Dhayal, V.; Kumar, U.; Hashmi, S. Z.; Sadhu, V.; Choudhary, B. L.; Kumar, S.; Saya, S.; Kuznetsov, A. E.; Dala, S.; Gupta, S. K.; Alvi, P. A. Structural, optical, and surface morphological studies of ethylv cellulose/graphene oxide nanocomposites. Polym. Compos. 2020, 41, 2792–2802.

(25) Papageorgiou, G. Z.; Terzopoulos, Z.; Achilias, D. S.; Bikisaris, D. N.; Kapnisti, M.; Gournis, D. Biodegradable poly(ethylene succinate) nanocomposites. Effect of filler type on thermal behaviour and crystallization kinetics. Polymer 2013, 54, 4604–4616.

(26) Avrami, M. Kinetics of phase change. II. Transformation-time relations for random distribution of nuclei. J. Chem. Phys. 1940, 8, 212–224.

(27) Avrami, M. Granulation, phase change, and microstructure kinetics of phase change. III. J. Chem. Phys. 1941, 9, 177–184.
(28) Jeziorny, A. Parameters characterizing the kinetics of the non-isothermal crystallization of poly(ethylene terephthalate) determined by d.s.c. *Polymer* 1978, 19, 1142−1144.
(29) Ozawa, T. Kinetics of non-isothermal crystallization. *Polymer* 1971, 12, 150−158.
(30) Liu, T.; Mo, Z.; Wang, S.; Zhang, H. Nonisothermal melt and cold crystallization kinetics of poly(aryl ether ether ketone ketone). *Polym. Eng. Sci.* 1997, 37, 568−575.
(31) Aulitwan, A.; Woo, E. M. Crystallization kinetics and degradation of nanocomposites based on ternary blend of poly(L-lactic acid), poly(methyl methacrylate), and poly(ethylene oxide) with two different organoclays. *J. Appl. Polym. Sci.* 2012, 125, No. E444.
(32) Yang, C. -T.; Lee, L. -T.; Wu, T. -Y. Isothermal and nonisothermal crystallization kinetics of poly(ε-caprolactone) blended with a novel ionic liquid, 1-ethyl-3-propylimidazolium bis(trifluoromethanesulfonfyl)imide. *Polymers* 2018, 10, 543.
(33) Papageorgiou, G. Z.; Terzopoulou, Z.; Bikiaris, D.; Triantafyllidis, K. S.; Diamanti, E.; Gournis, D.; Klonos, P.; Giannoulidis, E.; Pissis, P. Evaluation of the formed interface in biodegradable poly(L-lactic acid)/graphene oxide nanocomposites and the effect of nanofillers on mechanical and thermal properties. *Thermochim. Acta* 2014, 597, 48−57.
(34) Dobreva, A.; Gutzow, I. Activity of substrates in the catalyzed nucleation of glass-forming melts. I. Theory. *J. Non-Cryst. Solids* 1993, 162, 1−12.
(35) Dobreva, A.; Gutzow, I. Activity of substrates in the catalyzed nucleation of glass-forming melts. II. Experimental evidence. *J. Non-Cryst. Solids* 1993, 162, 13−25.
(36) Papageorgiou, D. G.; Papageorgiou, G. Z.; Bikiaris, D. N.; Chrissafis, K. Crystallization and melting of propylene-ethylene random copolymers. Homogeneous nucleation and β-nucleating agents. *Eur. Polym. J.* 2013, 49, 1577−1590.
(37) Nerantzaki, M.; Papageorgiou, G. Z.; Bikiaris, D. N. Effect of nanofiller’s type on the thermal properties and enzymatic degradation of poly(ε-caprolactone). *Polym. Degrad. Stab.* 2014, 108, 257−268.
(38) Papageorgiou, D. G.; Chrissafis, K.; Pavlidou, E.; Deliyanni, E. A.; Papageorgiou, G. Z.; Terzopoulou, Z.; Bikiaris, D. N. Effect of nanofiller’s size and shape on the solid state microstructure and thermal properties of poly(butylene succinate) nanocomposites. *Thermochim. Acta* 2014, 590, 181−190.
(39) Friedman, H. L. Kinetics of thermal degradation of char-forming plastics from thermogravimetry. Application to a phenolic plastic. *J. Polym. Sci., Part C: Polym. Symp.* 1964, 6, 183−195.
(40) Vassiliou, A. A.; Papageorgiou, G. Z.; Achilias, D. S.; Bikiaris, D. N. Non-isothermal crystallisation kinetics of in situ prepared poly(ε-caprolactone)/surface-treated SiO2 nanocomposites. *Macromol. Chem. Phys.* 2007, 208, 364−376.