

Crystallization Properties of Polycaprolactone Composites Filled With Nanometer Calcium Carbonate

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ABSTRACT: Polycaprolactone (PCL) composites filled with nanometer calcium carbonate (nano-CaCO₃) were prepared by means of a twin-screw extruder in this study. The nano-CaCO₃ surface treated with stearate. The crystalline properties of the PCL/nano-CaCO₃ composites were measured with a differential scanning calorimeter to identify the influence of the nanometer filler content on the crystalline properties. The results show that the crystallization onset temperature, crystallization temperature, and crystallization end temperature of the composites were obviously higher than those of the unfilled PCL resin, and the crystallization degree (χ_c) of the composites increased with increasing particle weight fraction (ϕ_f) when ϕ_f was more than 1%. When ϕ_f was 1%, χ_c of the composite was less than that of the unfilled PCL resin. Moreover, the dispersion of the inclusions in the matrix was observed by means of scanning electron microscopy. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

KEYWORDS: composites; crystallization; differential scanning calorimetry (DSC); nanostructured polymers

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INTRODUCTION

Polycaprolactone (PCL) is one of the most interesting biodegradable polymeric materials; it has good biodegradable and mechanical properties. Biodegradable polymers have been widely used for the production of bags, sacks, and food packaging because these polymers, prepared from renewable resources, can undergo biodegradation upon disposal.¹ To further improve the processing and mechanical properties, PCL is usually modified by blending with other resins or filling with inorganic particles. Since the 1990s, PCL blend systems have been studied extensively; these have included poly(vinyl chloride)/PCL,² styrene acrylonitrile/PCL,³ poly(butylene terephthalate)/PCL,⁴ and polystyrene/PCL⁵ binary blend systems, and poly(epsilon-caprolactone)/poly(3-hydroxybutyrate-co-3-hydroxyhexanoate)/PCL blend systems.⁶ Recently, a number of studies on the fabrication and characterization of inorganic particle-filled PCL composites have been made.^{1,7–9} Roohani-Esfahani and et al.⁸ investigated the effects of bioactive glass nanoparticles on the mechanical and biological behavior of composite-coated scaffolds. Xiao et al.⁹ researched the electroactive shape memory properties of poly(epsilon-caprolactone)/functionalized multiwalled carbon nanotube nanocomposites.

For inorganic rigid-particle-filled polymer composites, the physical and mechanical properties depend, to a great extent, upon interfacial morphology, such as the interfacial adhesion between the filler and the matrix, the interfacial structure, the dispersion of the inclusions in the matrix, and the crystalline properties.^{10–13} It is generally believed that the crystallization behavior is closely related to the physical and mechanical properties for crystallizable polymeric materials. In general, the effects of the filler content, size, and shape on the crystallization behavior are significant. In a previous work, Liang et al.¹⁴ studied the crystallization properties of glass bead filled low-density polyethylene composites. Siqueira et al.¹⁵ investigated the impact of the nature and shape of cellulosic nanoparticles on the isothermal crystallization kinetics of poly(epsilon-caprolactone) and found that the crystallization of microbial fuel cell nanocomposites was slightly faster than that of CNW nanocomposites. Liu et al.¹⁶ studied the nonisothermal crystallization kinetics of poly(epsilon-caprolactone)/zinc oxide (ZnO) nanocomposites (PCLZS) with high ZnO contents. The results show that the crystallization activation energies of PCLs with three different ZnO contents were nearly identical within the tolerance, which further demonstrated that the effect of the ZnO content on the

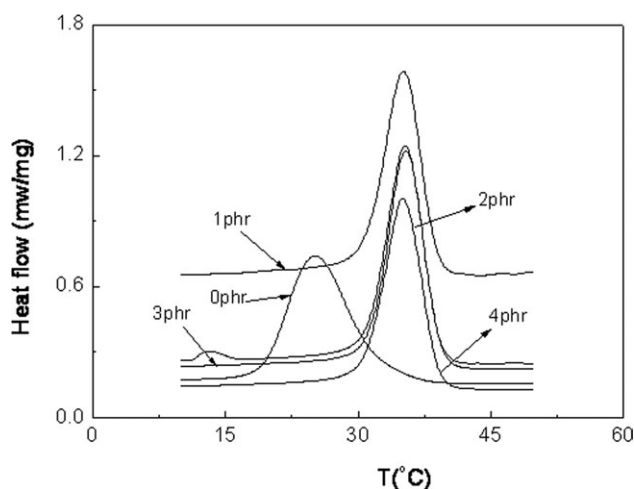


Figure 1. DSC curves of the PCL/nano-CaCO₃ composite systems (T = temperature).

crystallization behaviors was small when the ZnO content in the PCLZs was high. Moreover, some researchers have studied the crystallization kinetics of PCL composites, such as modified bamboo fiber/PCL composites¹⁷ and silk fibroin fiber-reinforced poly(epsilon-caprolactone) biocomposites.¹⁸

More recently, Liang et al.¹⁹ measured the melt flow properties in the capillary extrusion of nanometer calcium carbonate (nano-CaCO₃) filled PCL biocomposites. Our objectives in this study were to investigate the influence of the nano-CaCO₃ content on the crystallization properties of the PCL/nano-CaCO₃ composites under experimental conditions.

EXPERIMENTAL

Raw Materials

A biodegradable resin, PCL with the trademark PCL6800, serving as a matrix material was supplied by Shenzhen Bright China Industrial Co., Ltd. (Shenzhen city, China). Its melt flow rate and density were 10.3 g/10 min and 1.09 g/cm³, respectively. The filler was nano-CaCO₃ particles, produced by Anyuan Scientific and Technological Chemical Plant (Anyuan city, China). The mean diameter of the particle was 40 nm, and its density was 2.55 g/cm³.

Composite Preparation

The nano-CaCO₃ particles were surface-pretreated with stearic acid. The mixture of the surface-treated particles with the PCL resin was carried out in a high-speed compounding machine (Zhangjiagang city, China). The mixture was then melt-blended in a twin-screw extruder (Nanjing city, China) at a screw speed of 25 rpm and a temperature of 100–140°C. The diameter of the screw was 35 mm, and its length-to-diameter ratio was 40. The composite extrudate was subsequently chopped into granules. Composites with four different weight fractions of filler particles ($\phi_f = 1, 2, 3,$ and 4%) were studied. Finally, the fabricated composites were dried at 60°C for 5 h before crystallization property testing.

Instrument and Methodology

The crystallization properties of the PCL/nano-CaCO₃ ternary composites were measured with a differential scanning calorimeter (model DSC204) supplied by Netzsch Co. (Selb, Germany).

The test temperature range was 0–100°C, the heat preservation time was 5 min, and the heating rate was 3°C/min.

The impact fracture surfaces of the specimens from the experiments were examined by means of scanning electron microscopy (SEM; model S-3700N, Hitachi Instrument Co., Tokyo, Japan) to observe the filler dispersion or distribution in the PCL matrix. The specimens were gold-coated before SEM examination.

RESULTS AND DISCUSSION

Differential Scanning calorimetry (DSC) Curves

The DSC curve presents the correlation between the heat flow and the temperatures of the materials. Figure 1 shows the DSC curves of the unfilled PCL resin (i.e., 0 phr or phr = 0) and the PCL/nano-CaCO₃ composite systems. In Figure 1, phr represents the parts per hundred parts of PCL resin by weight. It can be seen that the height and width of the peaks of the DSC curves varied with increasing nano-CaCO₃ content, but this variation was irregular. The location of the peaks of the composites moved right to the unfilled PCL resin as the reference, whereas the area of crystalline peak increased with increasing concentration of the nano-CaCO₃.

The area of the crystalline peak of the DSC curve presents the crystallization properties of polymeric materials. Therefore, this meant that the addition of the nano-CaCO₃ in the PCL resin was beneficial for improving the crystallization properties of the PCL composites. In other words, the nano-CaCO₃ particles played the role of the heterogeneous nucleation in the PCL matrix.

Crystallization Onset Temperature (T_s)

T_s is the temperature in which the crystallization starts in the crystalline materials. T_s is an important parameter that demonstrates the crystallization properties of the polymeric materials. Figure 2 illustrates the relationship between T_s of the unfilled PCL resin and the filled PCL composite systems and the weight fraction of the nano-CaCO₃. We observed that T_s of the filled PCL composite system with ϕ_f of 1% was obviously higher than that of the unfilled PCL resin (i.e., $\phi_f = 0$). Then, it increased slightly with increasing ϕ_f . This indicated that the addition of

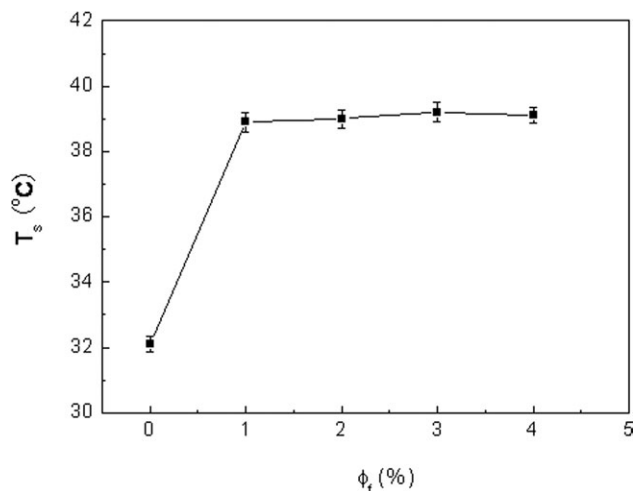


Figure 2. Relationship between the beginning T_c and nano-CaCO₃ weight fraction.

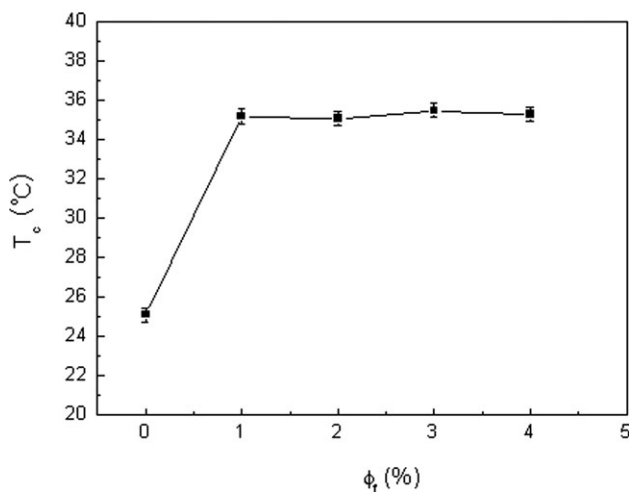


Figure 3. Correlation between T_c and the nano- CaCO_3 weight fraction.

nano- CaCO_3 increased T_s of the filled PCL composites. In other words, T_s of the filled PCL composites was moved up when the PCL was filled with the nano- CaCO_3 .

As stated previously, the nano- CaCO_3 particles play the role of heterogeneous nucleation in the PCL matrix, it is beneficial to start the crystallization of the composite melts, even though at higher temperature, it leads to an increase in T_s of the filled PCL composites.

Crystallization Temperature (T_c)

T_c is the temperature at the peak of the DSC curve, it is also an important parameter and demonstrates the crystallization properties of the polymeric materials. Figure 3 presents the correlation between T_c of the unfilled PCL resin and the filled PCL composite systems and the weight fraction of the nano- CaCO_3 . Similar to the results shown in Figure 2, T_c of the filled systems with ϕ_f of 1% increased suddenly; then, the variation of T_c was slight with increasing ϕ_f . This indicated that the addition of nano- CaCO_3 increased T_c of the filled PCL composites. In other words, T_c of the filled PCL composites moved up when the PCL was filled with the nano- CaCO_3 .

Because the nano- CaCO_3 particles played the role of heterogeneous nucleation in the PCL matrix and it was beneficial for starting the crystallization of the composite melts, the beginning T_c of the filled PCL composites increased correspondingly; this resulted in a rise in T_c of the filled PCL composites.

Crystallization End Temperature (T_e)

T_e is the temperature at which crystallization ends in crystalline materials. T_e is also an important parameter that demonstrates the crystallization properties of the polymeric materials. Figure 4 displays the dependence of the T_e 's of the unfilled PCL resin and the filled PCL composite systems on the weight fraction of the nano- CaCO_3 . Similar to the results shown in Figures 2 and 3, T_e 's of the filled systems with ϕ_f 's of 1% increased quickly; then, the variation of T_e was slight with increasing ϕ_f . This indicated that the addition of the nano- CaCO_3 increased T_e of the filled PCL composites. In other words, T_e of the filled PCL composites moved up when the PCL was filled with the nano- CaCO_3 .

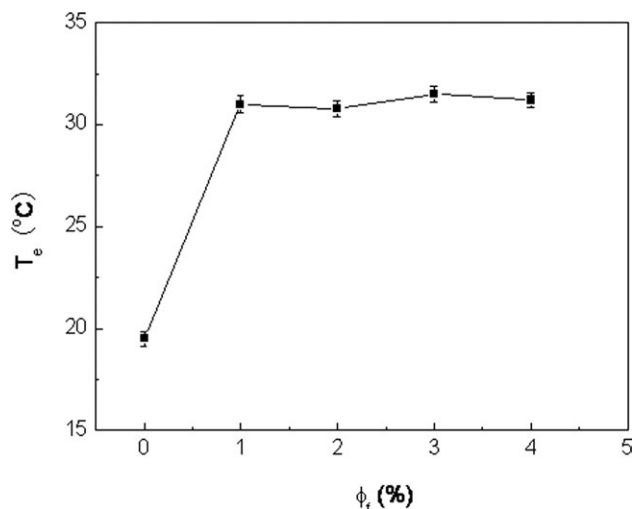


Figure 4. Dependence of the ending T_c on the nano- CaCO_3 weight fraction.

T_c Interval

The T_c interval is defined as the temperature zone from the beginning T_c to the ending T_c of the materials; it characterizes the temperature history of crystallization for materials. Figure 5 shows the dependence of the crystallization temperature interval (T_i) of the unfilled PCL resin and the filled PCL composite systems on the weight fraction of the nano- CaCO_3 . It was also found that the temperature interval of the composite decreased suddenly when the nano- CaCO_3 weight fraction was 1%; then, it varied slightly with increasing filler weight fraction. This indicated that the temperature history of crystallization for the composites decreased with the addition of the nano- CaCO_3 .

Crystalline Degree (χ_c)

χ_c is an important index for the characterization of the crystallization properties of materials. The χ_c of polymeric materials is usually defined as follows:

$$\chi_c = (\Delta H_c / \Delta H^*) \times 100\% \quad (1)$$

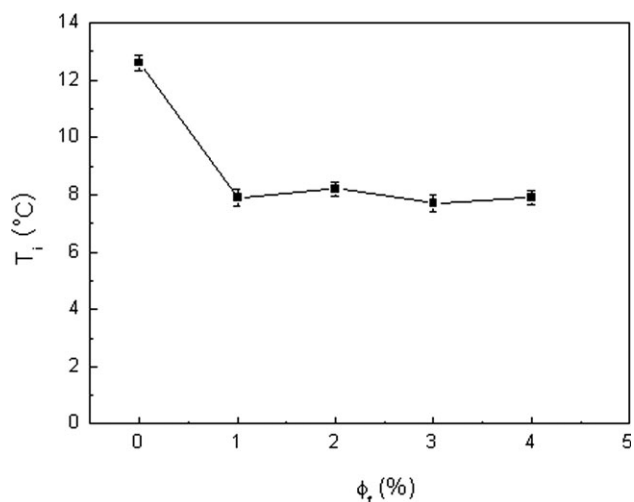


Figure 5. Dependence of T_i on the nano- CaCO_3 weight fraction.

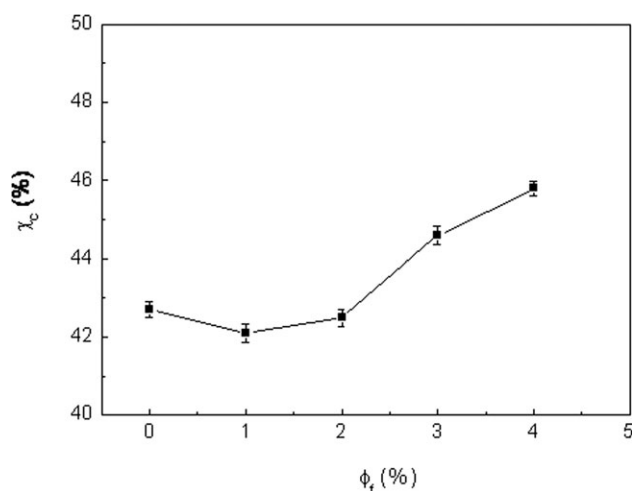


Figure 6. Relationship between χ_c and the nano- CaCO_3 weight fraction.

where ΔH_c is the thermal enthalpy during the crystallization of the composite and ΔH^* is the thermal enthalpy in crystallization of the neat PCL resin ($\Delta H^* = 135.31 \text{ J/g}$).

On the basis of the experimental measurement data and eq. (1), the χ_c 's of the PCL/nano- CaCO_3 composites were determined. Figure 6 shows the relationship between the χ_c of the unfilled PCL resin and the filled PCL composite systems and the weight fraction of the nano- CaCO_3 . We observed that the χ_c of the composite with $\phi_f = 1\%$ was less than that of the unfilled PCL resin; then, the χ_c values of the composites increases with increasing filler weight fraction. This means that the nano- CaCO_3 particles may not have played the role of heterogeneous nucleation in the PCL matrix when the concentration of the nano- CaCO_3 was low.

Discussion

Crystallization is the formation and development process of a crystal. Therefore, it is generally believed that the crystallization properties depend, to a great extent, on the effect of heterogeneous nucleation of the filler in the matrix for inorganic particu-

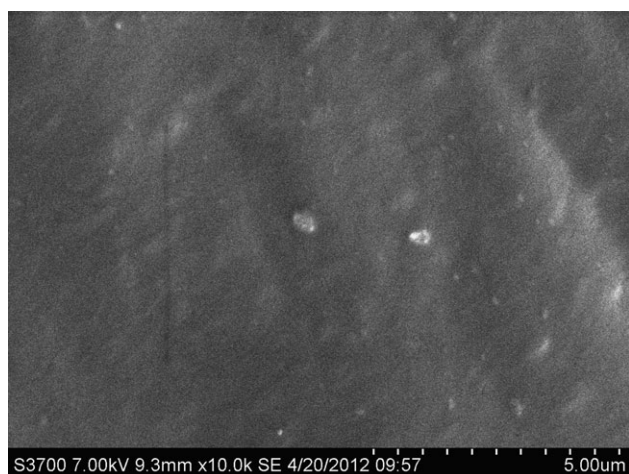


Figure 7. SEM photograph of the fracture surface of the PCL/nano- CaCO_3 composite ($\phi_f = 1\%$).

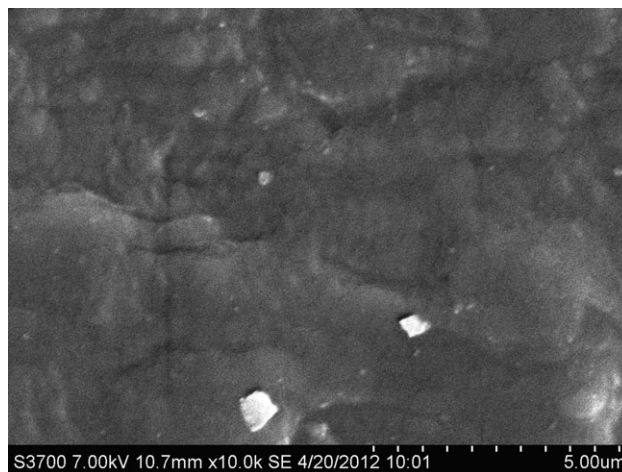


Figure 8. SEM photograph of the fracture surface of the PCL/nano- CaCO_3 composite ($\phi_f = 2\%$).

late-filled polymer composites. In the case of a low concentration of the nano- CaCO_3 , χ_c of the composite decreased when the weight fraction was 1% (see Figure 6). This demonstrated that the role of the nucleation agent of the nano- CaCO_3 particles in the matrix was not obvious. With a further increase in the concentration of the nano- CaCO_3 particles, χ_c of the PCL composites increased. The reasons were as follows: on the one hand, the nano- CaCO_3 particles were beneficial in the promotion of the crystalline speed because of their nucleation agent effect, and on the other hand, the movement of the PCL molecular chains were limited, and the molecular chains for crystallization were reduced. As a result, χ_c increased slightly with increasing nano- CaCO_3 weight fraction (see Figure 6).

During the past decade, the heterogeneous nucleation effect of inorganic particles in polymer composites has been paid extensive attention. Jana and Im²⁰ studied the isothermal crystallization behavior of PCL/functionalized multiwalled carbon nanotube composites using DSC and found a heterogeneous nucleation in the crystallization growth process. Dong et al.²¹



Figure 9. SEM photograph of the fracture surface of the PCL/nano- CaCO_3 composite ($\phi_f = 3\%$).

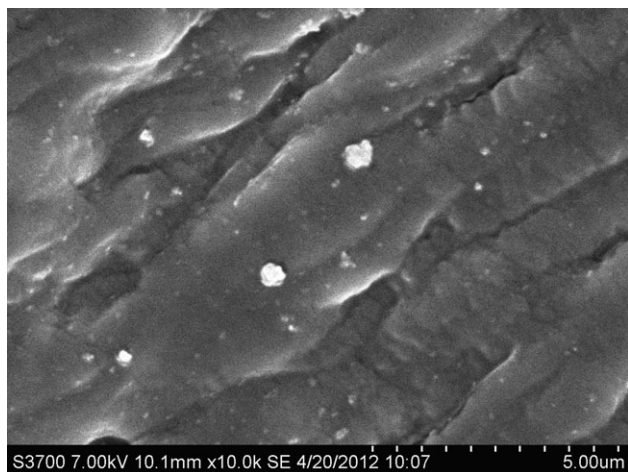


Figure 10. SEM photograph of the fracture surface of the PCL/nano-CaCO₃ composite ($\phi_f = 4\%$).

investigated the crystallization behavior and mechanical properties of poly(epsilon-caprolactone)/cyclodextrin biodegradable composites and found that the addition of inclusion complex greatly increased the crystallization rate and thermal stability of the PCL.

In general, the crystallization properties of inorganic particulate-filled polymer composites are closely related to the dispersion or distribution of the inclusions in the matrix. In addition, they depend, to a great extent, on the effect of the heterogeneous nucleation of the filler in the matrix. Figure 7 shows the SEM photograph of the fracture surface of the PCL/nano-CaCO₃ composite with a ϕ_f of 1%. Figure 8 shows the SEM photograph of the fracture surface of the PCL/nano-CaCO₃ composite with a ϕ_f of 2%. Figure 9 shows the SEM photograph of the fracture surface of the PCL/nano-CaCO₃ composite with a ϕ_f of 3%. Figure 10 shows the SEM photograph of the fracture surface of the PCL/nano-CaCO₃ composite with a ϕ_f of 4%. We could see that the dispersion and distribution of the nano-CaCO₃ in the PCL matrix were roughly uniform, even in the case of a higher filler concentration, such as $\phi_f > 1\%$. As discussed previously, when the filler particles played the role of heterogeneous nucleation in the PCL matrix, the particle surface was like the nucleation agent, χ_c in the interfacial layer between the filler and matrix was higher than in the other places in this case. The more uniform the dispersion of the inclusions was in the matrix, the higher the interfacial layer volume was, and the higher the χ_c of the composite was. Consequently, χ_c of the PCL/nano-CaCO₃ composites increased with increasing filler weight fraction when ϕ_f was more than 1% (see Figure 6).

CONCLUSIONS

The effects of the nano-CaCO₃ particles on the T_s , T_e , and T_c values of the PCL/nano-CaCO₃ composites were significant. The results show that T_s , T_e , and T_c of the PCL/nano-CaCO₃ composites were obviously higher than those of the unfilled PCL resin, whereas T_i of the PCL/nano-CaCO₃ composites was obviously lower than that of the unfilled PCL resin. Then, they varied slightly with increasing filler weight fraction.

χ_c of the PCL/nano-CaCO₃ composites increased with increasing weight fraction of nano-CaCO₃ when ϕ_f was higher than 1%. This could be attributed to the role of the heterogeneous nucleation of nano-CaCO₃ in the PCL matrix and the uniform dispersion of the filler in the matrix. When the weight fraction of the nano-CaCO₃ was equal to 1%, χ_c of the PCL/nano-CaCO₃ composites was less than that of the unfilled PCL resin. This indicated that the nano-CaCO₃ particles might not have played the role of the heterogeneous nucleation in the PCL matrix in the case of a low concentration of nano-CaCO₃.

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REFERENCES

1. Shalumon, K. T.; Anulekha, K. H.; Chennazhi, K. P.; Tamura, H.; Nair, S. V.; Jayakumar, R. *Int. J. Biol. Macromol.* **2011**, *48*, 571.
2. Mareau, V. H.; Prud'homme, R. E. *Macromolecules* **2003**, *36*, 675.
3. Ketklaars, A. A. J.; Papantoniou, Y.; Nakayma, K. *J. Appl. Polym. Sci.* **1997**, *66*, 921.
4. Di Lorenzo, M. L.; La Pietra, P.; Errico, M. E.; Righetti, M. C.; Angiuli, M. *Polym. Eng. Sci.* **2007**, *47*, 323.
5. Felker, F. C.; Biresaw, G. J. *Biobased Mater. Bioenergy* **2007**, *1*, 401.
6. Katsumata, K.; Saito, T.; Yu, F.; Nakamura, N.; Inoue, Y. *Polym. J.* **2011**, *43*, 484.
7. Liu, J. Y.; Reni, L.; Wei, Q.; Wu, J. L.; Liu, S.; Wang, Y. J.; Li, G. Y. *Express Polym. Lett.* **2011**, *5*, 742.
8. Roohani-Esfahani, S. I.; Nouri-Khorasani, S.; Lu, Z. F.; Appleyard, R. C.; Zreiqat, H. *Acta Biomater.* **2011**, *7*, 1307.
9. Xiao, Y.; Zhou, S. B.; Wang, L.; Gong, T. *Am. Chem. Soc. Appl. Mater. Interface* **2010**, *2*, 3506.
10. Lu, S.; Yan, L.; Zhu, X.; Qi, Z. *J. Mater. Sci.* **1992**, *27*, 4633.
11. Guild, F. J.; Young, F. J. *J. Mater. Sci.* **1989**, *24*, 2454.
12. Meddad, A.; Fisa, B. *J. Appl. Polym. Sci.* **1997**, *65*, 2013.
13. Hui, C. Y.; Hia, D. *Polym. Eng. Sci.* **1998**, *38*, 774.
14. Liang, J. Z.; Li, R. K. Y.; Tjong, S. C. *J. Appl. Polym. Sci.* **1999**, *71*, 687.
15. Siqueira, G.; Frascini, C.; Bras, J.; Dufresne, A.; Prud'homme, R.; Laborie, M. P. *Eur. Polym. J.* **2011**, *47*, 2216.
16. Liu, Q. S.; Deng, B. Y.; Zhu, M. F.; Shyr, T. W.; Shan, G. F. *J. Macromol. Sci. Phys.* **2011**, *50*, 2366.
17. Huang, Y. Y.; Liu, H. X.; He, P. S.; Yuan, L.; Xiong, H. G.; Xu, Y. M.; Yu, Y. *J. Appl. Polym. Sci.* **2010**, *116*, 2119.
18. Qiao, X. Y.; Li, W.; Sun, K.; Chen, X. D. *Polym. Int.* **2010**, *59*, 447.
19. Liang, J. Z.; Zhou, L.; Tang, C.-Y.; Tsui, C. P.; Li, F. J. *Polym. Test.* **2012**, *31*, 149.
20. Jana, R. N.; Im, C. *Int. J. Polym. Anal. Character.* **2009**, *14*, 418.
21. Dong, T.; Mori, T.; Pan, P. J.; Kai, W.; Zhu, B.; Inoue, Y. *J. Appl. Polym. Sci.* **2009**, *112*, 2351.