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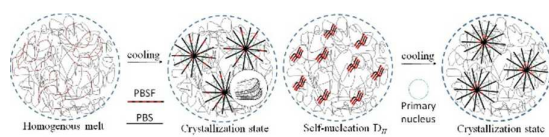
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Graphical Abstract

A new method has been invented to control the spherulite growth rate of isothermally crystallized PBS without changing its molecular composition.





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How to regulate the isothermal growth rate of polymer spherulite without changing its molecular composition? †

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Yi-Ren Tang, Yang Gao, Jun Xu* and Bao-Hua Guo*

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Poly(butylene succinate-co-butylene fumarate) (PBSF) can work as a highly efficient polymeric nucleating agent for poly(butylene succinate) (PBS) basing on epitaxial crystallization, namely matching of crystal lattice. Benefiting from the unique behavior that PBSF can enhance the spherulite growth rate (G) of PBS, a new method combining addition of a fixed content of PBSF and self-nucleation has been proposed to regulate G of isothermally crystallized PBS for the first time.

For semi-crystalline polymer, the crystallization behavior determines its mechanical properties, thermal deformation properties, transparency, and chemical resistance primarily.¹ However, the crystallization behaviour of polymer is far more complex than small molecule for the two reasons: (a) the diffusion barrier energy is high due to the long chain characteristic of polymer and the interaction between molecular chains. (b) polymer prefers to form imperfect crystal for the reason of heterogeneity of the structure, the wide distribution of molecular weight, and the long relaxation time of polymer chain during crystallization.² Therefore, it is very important for researchers and industry to clarify the crystallization behaviour and further increase the crystallization rate of polymer.

Nucleating agents (NAs) have been widely used in the polymer manufacturing process for their advantages of low content, increase of mechanical properties and crystallization rate, transparency, and a shortened molding cycle time.³⁻¹⁰ The vast majority of the NA increases the crystallization rate only by improving the primary nucleation rate rather than the secondary nucleation rate, as a result, the spherulite growth rate (G) almost remains constant.¹¹ However, basing on the isomorphism, our previous reports^{12,13} have developed a totally new polymeric NA, poly(butylene succinate-co-butylene fumarate) (PBSF) for poly(butylene succinate) (PBS), which is a widely used biodegradable polymer in the industry. Interestingly, these

polymeric NAs improved the G of PBS significantly without changing the crystallization regime. The polymeric NA offers us a new method to control the secondary nucleation rate as well as primary nucleation rate through altering its content. To promote our research deeply, a new question is arisen. Is there any other possibility to regulate the secondary nucleation rate at the same isothermal crystallization temperature without changing the composition of the polymer?

The unmelted crystallites and/or nuclei are the ideal NA for the polymer itself because of the identical crystal lattice and the favourable interfacial interaction.¹⁴ Self-nucleation (SN) method is very important in probing the nucleation mechanism of homopolymer,¹⁵⁻¹⁷ copolymer,¹⁸⁻²⁰ and nanocomposites,²¹⁻²² which is originally introduced by Fillon et al.^{23,24} Basing on the crystallization temperature (T_c) during cooling after SN at different temperature (T_s) (Corresponding DSC procedure is shown in ESI,† Figure S1.), the crystallization behavior of polymer can be divided into three domains. In (Domain I) D_I , all the crystals have been melted completely, and polymer melted at different temperatures have the same T_c under the same cooling procedure. As the melting temperature decreases, the major crystals have been melted with a few tiny crystals or nuclei remained, the SN phenomenon occurs and it is called Domain II (D_{II}). The characteristic of D_{II} is that T_c increases progressively and the nucleation density also increases enormously as T_s decreases. With the melting temperature further decreases, the majority of the crystals experience annealing and only thinner lamellae have been melted. Thus T_c remains unchanged and double melting peaks appear. This temperature range of T_s is termed Domain III (D_{III}).

Here we report a novel strategy to tune the secondary nucleation rate of PBS by combining PBSF which promotes the secondary nucleation rate of PBS and SN method. PBS, PBSF 40 (the number means the feeding molar ratio of fumarate content), and PBSF 60 have been synthesized through polycondensation method. The comonomer composition in PBSF copolymers was calculated from ¹H-NMR (Figure S2) and summarized in Table S1. Films of the blend samples, PBS+PBSF 40 1wt% and PBS+PBSF 60 1wt% (denoted as P-40 and P-60) are prepared by solution casting method. The experimental details were given in ESI†. Figure 1 shows the

Advanced Materials Laboratory of Ministry of Education, Department of Chemical Engineering, Tsinghua University, Beijing 100084, China.

E-mail: jun-xu@tsinghua.edu.cn Tel: +86-10-62784740

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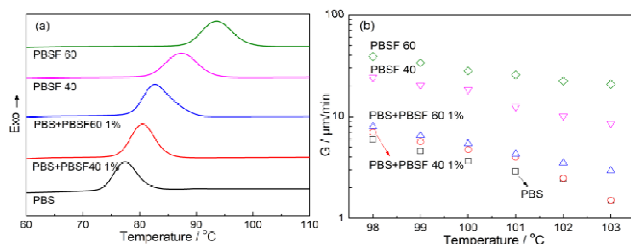


Fig. 1 (a) DSC cooling curves of PBS, PBF, and blend samples at the cooling rate of 10 °C/min after melted at 160 °C for 5min; (b) G of different samples at various crystallization temperatures after melted at 160 °C for 5min.

nonisothermal melt-crystallization temperature and G of the different samples. The random copolymer PBF possesses higher primary and secondary nucleation ability than PBS. This is because the fumarate units take trans conformation naturally in PBF while the succinate units adopt trans conformation only in PBS crystal lattice. During crystallization the conformational entropy change of PBF will reduce as more fumarate units exist in the backbone of the polymer chain. Moreover, the melting enthalpy keeps almost constant. Thus the crystallization ability of PBF is positively associated with the fumarate content.¹² Due to the matching of crystal lattice (Figure 2), the copolymer can act as a highly efficient polymeric nucleating agent, which increases the primary and secondary nucleation rate (a portion of PBF takes part in secondary nucleation) of PBS simultaneously, and the detailed nucleation mechanism was based on epitaxial nucleation.¹³ The crystallization half time ($t_{0.5}$) is a key parameter to evaluate the nucleation ability and characterize the overall crystallization kinetics.¹⁴ As shown in Figure S3, the $t_{0.5}$ of PBS reduces from 93 min to 30 min at 102 °C with the introduction of 1 wt% PBF 60. In summary, the PBF copolymers are prominent nucleating agent for PBS and the nucleation ability of PBF improves with the increase of fumarate ratio.

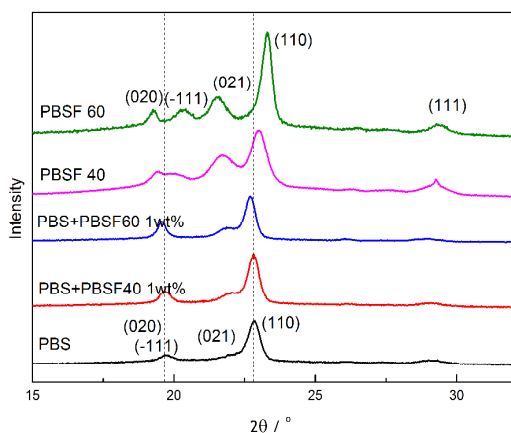


Fig. 2 WAXD patterns of neat PBS, PBF copolymers, and blend samples isothermally crystallized at 80 °C.

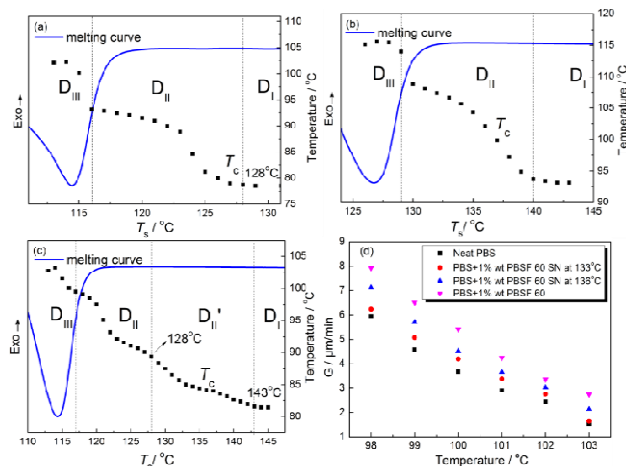


Fig. 3 Self-nucleation domains of the melting curve and the value of T_c with various T_s of (a) PBS, (b) PBF 60, (c) P-60; (d) G of PBS, P-60, and P-60 after SN treatment at various crystallization temperatures.

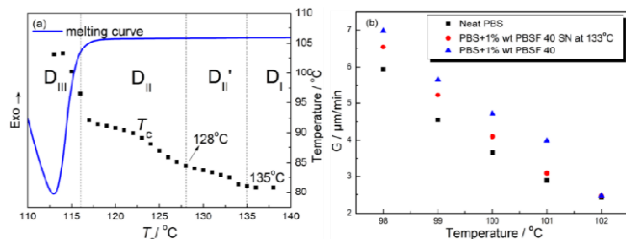


Fig. 4 (a) Self-nucleation domains of the melting curve and the value of T_c with various T_s of P-40; (b) G of PBS, P-40, and P-40 after SN treatment at various crystallization temperatures.

Figure 3 (a) and (b) show the SN behaviors of neat PBS and PBF 60. The temperature range of SN domain (D_{II}) of PBS and PBF 60 are 116–128 °C and 130–140 °C, respectively. The detailed procedure to obtain the value of T_c and G in the Figure 3 or 4 can be seen in the experiment section of ESI†. For the purpose of simplification, the DSC cooling curves after self-nucleation at various T_s s are not present here. Only the crystallization temperature T_c after SN has been presented in Figure 3 and 4. When the melting temperature is higher than 128 °C, the crystals are melted completely and T_c of PBS remains invariant. Thus we believe that the SN behavior of P-60 in the temperature range of 128–143 °C is due to the SN behavior of PBF 60 itself and is defined as D_{II}' , as shown in Figure 3(c). It's interesting that the melt-blending process window of PBS is approaching to D_{II} of PBF 60. This coincidence can be used to further increase and tailor T_c of PBS by regulating the process temperature. Moreover, the terminal temperature of D_{II}' increases as the fumarate content of the copolymer increases. This implies that our method can be used in various process methods, such as extrusion, film blowing, melt spinning, only by substituting the copolymer. Yin et al.¹⁴ also utilized poly(L-lactic acid) (PLLA) with high melting temperature to act as the nucleating agent for low molecular weight PLLA basing on SN mechanism. An astonishing result arises when we measure the G of blend samples after SN treatment at diverse temperatures. Figure 3(d) shows that the lower the SN temperature is, the lower G the blend sample has. On the contrary, T_c of PBS shifts to higher temperature. Figure 4

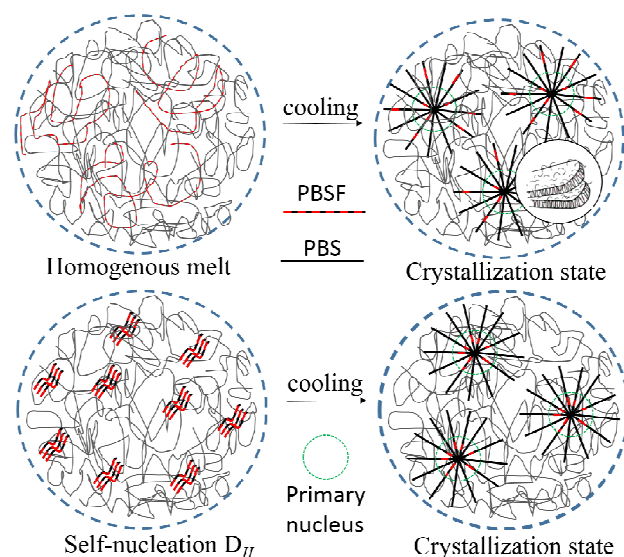


Fig. 5 Scheme of the “standard” melt-crystallization and “SN” melt-crystallization process. The black line represents PBS chain and the reddish black line is PBSF chain. The green circle (dotted line) represents primary nucleus.

exhibits the similar result in P-40 sample. The temperature range of D_{T_i} for P-40 is between 128–135 °C, which is narrower than that of P-60 for the less fumarate content and the lower melting point of PBSF40.

In our previous research, we have found that poly(butylene fumarate) (PBF) accelerates the secondary nucleation as well as the primary nucleation of PBS and thus enhances G of PBS. Compared to pure PBF, the smaller melting enthalpy of PBF in the blend sample of PBS+ 4wt% PBF reveals that a portion of PBF joins in the secondary nucleation of PBS instead of the primary nucleation.¹³ Therefore, the crucial role of the SN method in this work is to regulate the partition of PBSF between primary nucleation and secondary nucleation in order to control the G of PBS. When we focus on the high temperature range of the G , the increase ratio of P-40 and P-60 gets weaker and even levels off compared to pure PBS (Figure 3(d), 4(b)). This is a natural kinetic selection process of crystallization because PBSF has sufficient time to assembly to generate primary nucleus at low supercooling and fewer PBSF is remained for secondary nucleation. This means that the primary nucleation of PBS competes with the secondary nucleation of PBS in order to “invite” PBSF to join the nucleation and decrease the nucleation barrier. In low supercooling regime, more PBSF joined primary nucleation. However, we can increase the PBSF fraction for primary nucleation with the help of SN method in high supercooling regime. The mechanism of our method is that through changing the self-nucleation temperature T_s , the number of residual PBSF nuclei or PBSF chains with “memory effect” can be varied accordingly. In the condition of constant amount of PBSF, the residual PBSF for secondary nucleation will be reduce. These PBSF copolymers can form the primary nuclei fast after cooling to the crystallization temperature and lose the opportunity to join the secondary nuclei in the following crystallization process. Thus the PBSF fraction used for primary nucleation and secondary nucleation can be regulated

through SN method. The SN process had been schematically represented in Figure 5. The extreme condition that the copolymer in the blend sample completely forms the primary nuclei at sufficiently low T_s , as described in the bottom of Figure 5. Generally speaking, the lower the SN temperature, the more the PBSF primary nuclei, the higher the T_c and the lower the G .

The well-known Avrami^{25–27} equation is employed to study the effect of PBSF 60 and SN method on the isothermal crystallization kinetics of PBS. All the logarithmic curves have good linearity (Figure S4.), demonstrating that the Avrami equation is suitable to fit the isothermal crystallization after SN treatment. The Avrami exponent n of PBS increases from 1.5 to 2.6 after adding PBSF 60 and further shifts to 3.0 after SN experiment, as shown in Table S2. This implies that PBSF 60 might change the crystal growth mechanism and increase the growth dimensionality of PBS spherulites. For P-60, the value of n indicates typical spherulitic growth with heterogeneous nucleation and the result is further confirmed by polarized optical microscope (POM) study in Figure S5. The Lauritzen-Hoffman secondary nucleation theory²⁸ is used to analyze the different G value of P-60 at different SN temperatures. The nucleation constant K_g and the rate constant G_0 are calculated by using the empirical values of $U^* = 1500$ cal/mol and $T_\infty = T_g - 30$ K. The results are summarized in Table S3. All the data points for each sample can be fitted in one straight line, as presented in Figure S6. The results reported by Gan et al.²⁹ and our latest article¹³ found out that the transition from regime III to regime II and to regime I is at about 96 °C and 108 °C, respectively. This means that the addition of PBSF and SN method do not alter the crystallization regime and secondary nucleation mechanism of PBS. It's fairly interesting to find that the value of K_g and G_0 increase as the G increases. The detailed analysis of why the value of K_g and G_0 increase will be presented in our following article.

Conclusions

In summary, we have proposed a new method to regulate the spherulite growth rate of polymer without changing its composition. The partition of PBSF in primary nucleation and secondary nucleation at different SN temperatures is the crucial factor to control the G . For the isomorphous blend system in our article, the arbitrary G between the lower limit of PBS and upper limit of PBSF/PBF nucleated PBS can be obtained by elaborative choice of the T_s . Additionally, a preliminary study on the primary and secondary nucleation mechanism of PBS elucidates that our method may change the primary nucleation mechanism instead of secondary mechanism basing on the elevated Avrami exponent and invariable crystallization regime.

Acknowledgements

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