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Effects of Different Nucleating Agents, Annealing and Pre-stretching Process on the Crystallinity and Mechanical Properties of Poly(butylene carbonate)

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Electronic Supplementary Information

Abstract Poly(butylene carbonate) (PBC), a biodegradable aliphatic polycarbonate, is limited by its suboptimal thermal and mechanical properties. This study enhanced PBC by incorporating nanoscale nucleating agents combined with isothermal annealing and pre-stretching. The results indicate that the dispersion and interfacial interactions of different nucleating agents within the PBC matrix vary significantly. Among them, SiO_2 demonstrate good dispersion and compatibility, effectively enhancing the storage modulus and crystallization kinetics. Isothermal annealing and pre-stretching treatments further synergistically improved the crystallinity and mechanical performance of the composites: after annealing, the tensile strength of PBC/SiO_2 increased to 61.96 MPa, and after pre-stretching, it reached 83.26 MPa. Dynamic mechanical analysis and differential scanning calorimetry results consistently show that the incorporation of nucleating agents raises the glass transition temperature and thermal stability of the materials. This research provides systematic experimental evidence and process optimization strategies for the high-performance modification of PBC.

Keywords Poly(butylene carbonate); Pre-stretching; Isothermal annealing; Mechanical properties; Nucleating agent

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INTRODUCTION

The practical application of poly(butylene carbonate) (PBC) is hindered by its relatively limited thermomechanical properties and low tensile strength. To address this limitation, copolymerization and blending have been employed to enhance crystallization ability, thereby improving the overall performance. For instance, Kim *et al.* demonstrated the effectiveness of copolymerization using a series of PBC-based copolymers.[1–5] However, chemical copolymerization involves complex procedures and is less suitable for rapid and cost-effective industrial production of PBC films. Alternatively, incorporating nucleating agents offers a more straightforward approach to enhance crystallization and mechanical performance.[6–8]

To achieve balanced material properties, PBC are often introduced as soft segments. Wang *et al.* prepared PBS/PBC blends,[9] but observed poor compatibility between the two components, leading to island or bicontinuous morphologies depending on the composition. Although the crystallization rate of PBS increased with the PBC content and the impact strength improved significantly, compatibility remained a challenge. Li *et al.* developed PBC/sc-PLA blends *via* low-temperature melt-blending. At 20 wt% sc-PLA, stereocomplexation between $_L$- and $_D$-chains formed a percolated network structure, increasing the yield strength and modulus by 34% and 145%, respectively, compared to neat PBC.[10] Similarly, Wang *et al.* prepared PBC/PLA blends by melt processing.[11] At a PBC/PLA mass ratio of 1:9, the tensile strength reached 50.7 MPa. Blending polymers with inorganic particles is another effective strategy for the preparation of composite materials. Inorganic particles can act as nucleating agents, refining spherulite size, disrupting crystal regularity, and improving crystallization kinetics in semicrystalline polymers, thereby enhancing mechanical and surface properties. For example, Wang prepared PBC/SiO_2 composites *via* melt blending and found that well-dispersed SiO_2 improved mechanical performance,[12] crystallization behavior, and thermal stability. Zhu investigated talc, $CaCO_3$, BN, and h-BN as nucleating agents in PBC, reporting increased crystallization rates,[13] with BN showing the most pronounced effect. In PBC/talc systems, the crystallization rate increased with increasing talc content up to 4 wt%, beyond which it plateaued. Despite these studies, systematic reports on the mechanical properties of PBC blended with nucleating agents are limited.

Building upon our established findings that physical treat-

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ments (isothermal annealing and pre-stretching) effectively enhance crystallinity and induce crystal orientation in PBC, thereby improving its mechanical properties, this work proposes a hybrid modification strategy.[14,15] We hypothesized that coupling these physical treatments with nucleating agents will create dual reinforcement pathways: nanoparticle-triggered nucleation density elevation combined with crystal perfection/orientation control. To address this mechanistic synergy, we systematically investigated the following: (i) the role of inorganic nucleating agents in modulating PBC's crystallization kinetics, rheological behavior, and thermal stability of PBC; (ii) the synergistic interplay between nucleating agents and physical treatments (annealing/pre-stretching) on hierarchical crystalline structuring; and (iii) the consequent enhancement of bulk crystallinity and mechanical performance beyond standalone approaches.

EXPERIMENTAL

Materials

Poly(butylene carbonate) (PBC), synthesized *via* the melt transesterification polycondensation method with diphenyl carbonate (DPC), butanediol (BDO) as reactants, and MgO as a catalyst under a N_2 atmosphere in the laboratory according to a previous report,[16–18] has a number-average molecular weight of 6.25×10^4 g/mol, a weight-average molecular weight of 9.01×10^4 g/mol, and a molecular weight distribution index of 1.44. Fumed silica (SiO_2) nanoparticles with an average primary particle size of 7–40 nm were supplied by Macklin (Shanghai Macklin Biochemical Co., Ltd.). The magnesium oxide (MgO) nanoparticles with an average primary particle size of 30–50 nm were supplied by Macklin (Shanghai Macklin Biochemical Co., Ltd). The zinc oxide (ZnO) nanoparticles with an average primary particle size of 30 nm were supplied by Macklin (Shanghai Macklin Biochemical Co., Ltd). The titanium dioxide (TiO_2) nanoparticles with an average primary particle size of 25 nm were supplied by Macklin (Shanghai Macklin Biochemical Co., Ltd). The aluminium oxide (Al_2O_3) nanoparticles with an average primary particle size of 60 nm were supplied by Macklin (Shanghai Macklin Biochemical Co., Ltd). All materials were dried in a vacuum oven at 80 °C for 12 h.

Blending PBC with Inorganic Materials

The inorganic nucleating agent and PBC were weighed at a ratio of 1 wt% and added to the torque rheometer for blending. The test conditions of the torque rheometer were as follows: first zone, 100 °C; second zone, 100 °C; third zone, 100 °C; and speed, 30 r/min. PBC/inorganic particle composites were obtained by blending.

Preparation of PBC Composite Sheet

The PBC and the PBC composites were dried in a vacuum oven at 50 °C for 8 h. The dried polymer particles were then placed in a flat vulcanization bed machine. Dumbbell-shaped PBC specimens were prepared using the compression molding method. A platen vulcanizing press was employed at a processing temperature of 105 °C and pressure of 13 MPa.

Annealing Treatment

The samples were placed in a vacuum oven at 50 °C, annealed for 7 h for chain relaxation, and cooled to room temperature. After annealing, the samples were cooled and maintained at room temperature for 5 days before conducting the mechanical tests.

Pre-stretching Treatment

The prepared sheet was uniaxially stretched to 200% at a speed of 10 mm/min under the action of a universal stretching machine and maintained for 30 min under the uniaxial stress. A pre-stretched PBC sheet was obtained and cut into splines for mechanical testing.

Tensile-testing

The mechanical properties of the PBC dumbbell splines were tested using a universal testing machine (NKK 3010D) at a drawing speed of 50 mm/min at room temperature, and each value is the mean of 5 parallel samples.

Differential Scanning Calorimetry

The thermal properties of PBCs with and without annealing were characterized using differential scanning calorimetry (DSC). The instrument was calibrated using indium standard. Samples weighing 5–10 mg were heated from –60 °C to 100 °C at a rate of 10 °C/min under a N_2 atmosphere using a Model Q20 DSC (TA Instruments Inc., New Castle, DE, USA).

Isothermal crystallization kinetics: the PBC material was heated from –60 °C to 100 °C at a heating rate of 10 °C/min, maintained for 3 min, dropped sharply to the temperature of isothermal crystallization, maintained for 60 min, and then heated to 100 °C at a heating rate of 10 °C/min.

Thermogravimetric Analysis

The PBCs with and without annealing treatment (5–10 mg) were heated from to 30–600 °C under a nitrogen atmosphere at a heating rate of 10 °C/min, which was carried out with an STA 8000 (PerkinElmer, America) to measure the decomposition temperature of the materials.

Scanning Electron Microscopy

To obtain clear observations of the crystalline morphology, scanning electron microscopy (SEM) (ZEISS Sigma 360, Germany) was performed. The surface and cross section of the specimen were obtained from the fracture of the spline neck during the mechanical test. All the samples were sputter-coated with a thin layer of gold and observed at an accelerated voltage of 3 kV.

DMA

The storage modulus, loss modulus, and loss angle of the samples were measured using a DMA1-Mettler dynamic thermomechanical analyzer. In tensile mode, the size of the spline was 15 mm × 10 mm × 1 mm. The parameters were set as follows: heating rate, 3 °C/min; frequency, 1 Hz; amplitude 10.0 μm; and temperature scanning range, –60 °C to 40 °C.

Rheological Properties

The rheological properties of the blends were characterized using a rheological testing instrument (AR-G2, TA Instruments, USA). The sample was a 1.0 mm thick sheet. The test temperature was 150 °C, the shear angle frequency was 0.05–100 rad/s, and the strain was 2.5%.

RESULTS AND DISCUSSION

SEM Analysis of Poly(butylene carbonate)

To study the dispersion of different nucleating agents in PBC,

we systematically observed the cross-sectional morphology of PBC and its blends with different inorganic fillers (silica, alumina, titanium dioxide, magnesium oxide, zinc oxide, and calcium sulfate) to reveal the dispersion state, interface compatibility, and microstructure characteristics of fillers in the PBC matrix. The corresponding cross-sectional images are shown in Fig. 1. According to Fig. 1, the cross-section of the pure PBC sample shows a typical smooth and uniform fracture surface, which indicates that it has good toughness and uniformity. After adding different inorganic nucleating agents, PBC/SiO_2 showed good filler dispersion at 1 μm, and SiO_2 particles were evenly distributed in the PBC without obvious agglomeration, indicating good interface compatibility between the two. In PBC/ZnO composites, ZnO is uniformly dispersed in PBC, the interface is clear, and there is no obvious agglomeration, indicating that ZnO has good compatibility with PBC. A certain degree of TiO_2 filler agglomeration was observed at 1 μm for PBC/TiO_2, which may be related to the high surface energy of TiO_2 and the weak interface interaction with the PBC matrix. In PBC/Al_2O_3 composites, Al_2O_3 particles are closely combined with the matrix, and no obvious interface spalling phenomenon is observed, which indicates that Al_2O_3 particles have a certain enhancement effect on PBC. The obvious agglomeration of nucleating agents in the PBC/$TiO_2$and PBC/Al_2O_3 composites indicated that the distribution of nucleating agents in the composites was not uniform. At 1 μm, the distribution of MgO fillers in PBC/MgO is more uniform, closely integrated with the matrix, and has no obvious defects. PBC/$CaSO_4$ is uniformly distributed in the PBC matrix, and no large-scale agglomeration or interfacial debonding is observed, indicating that there is good interfacial bonding between $CaSO_4$ and PBC, which is expected to improve the mechanical properties of the material. In contrast, in the PBC/MgO and PBC/$CaSO_4$ composites, there are fewer nucleating agent particles in the bottom layer of the PBC, which also indicates that the material has an uneven distribution.

Rheological Properties

To explore the microstructure and relaxation behavior of a series of PBC composites, a dynamic frequency scanning test was performed. Figs. 2(a) and 2(b) show the relationship between the storage modulus and loss modulus of PBC at three different temperatures (100, 125, and 150 °C) and angular frequency. At all temperatures, the storage modulus and loss modulus depend on the angular frequency, which is a characteristic of viscoelastic behavior. At higher frequencies, the storage modulus is dominant, whereas the loss modulus is in a secondary position, which indicates that it is closer to the characteristics of the solid under rapid deformation conditions. In contrast, at lower frequencies, the loss modulus became more significant, indicating the existence of an enhanced viscous flow. As the temperature increases, the modulus curve moves toward a higher frequency, which is consistent with the time-temperature superposition principle. This shift reflects the acceleration of the molecular mobility and relaxation processes at higher temperatures. Fig. 2(c) shows the relationship between the storage modulus and loss modulus of the PBC composites at 150 °C and the angular frequency (ω).

The storage modulus of PBC and its composites tends to converge in the high-frequency region, which indicates that the response of the material to the outside world at high frequencies depends on its own motion and local interactions, and all materials are similar. However, in the low-frequency region (ω<10 rad/s), PBC composites show significant differences owing to the different rheological phenomena of their internal structures.[19,20] As shown in Fig. 2(c), both PBC/SiO_2 and PBC/ZnO exhibit a slightly higher storage modulus than neat PBC, which may be because the surfaces of SiO_2 and ZnO are rich in polar groups (—OH, *etc.*), which can form strong hydrogen bonds with —C=O in the PBC molecular chain or generate dipole-dipole interactions to achieve good stress transfer. Given the morphology of the composite material, the uniform dispersion of the nucleating agent helps form an effective network, limits chain segment mobility, increases friction between molecular chains, and improves the modulus. The modulus of PBC/MgO and PBC/$CaSO_4$ is slightly lower than that of PBC, and MgO and $CaSO_4$ may have problems with moisture absorption or compatibility with the matrix, so that the two fail to form a strong interface bonding, and the modulus of PBC/TiO_2 and PBC/Al_2O_3 is significantly lower than that of the matrix, which indicates that the interface between the nucleating agent and the matrix is extremely poor. Among these, Al_2O_3 agglomerates to form defects and becomes a stress concentration point.[21] The surface polarity of TiO_2 is too strong to effectively adhere to PBC, resulting in a decrease in the overall stiffness of the composite.

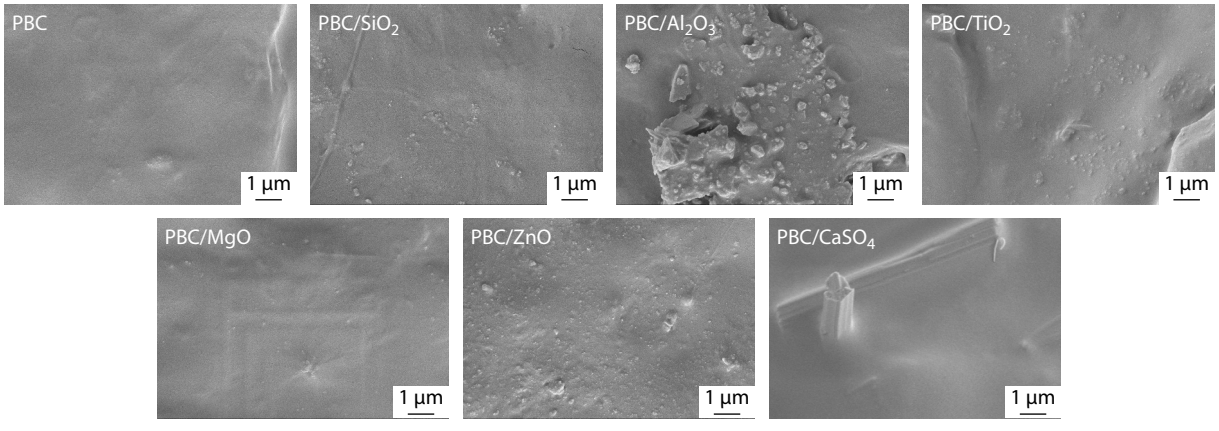

Fig. 1 The scanning electron microscope cross-section of PBC composites.

Thermogravimetric Analysis

The TG and DTA curves of the different PBC composites are shown in Fig. 3, and their corresponding thermal decomposition temperatures are listed in Table S1 (in the electronic supplementary information, ESI). Combined with the relevant data, it can be clearly seen that the thermal decomposition temperature of the PBC composites is significantly higher than that of pure PBC. For example, the thermal decomposition temperature of pure PBC increased from 296 °C for neat PBC to 310 °C for PBC/ZnO, and the maximum thermal decomposition temperature increased from 322 °C for PBC to 348 °C for PBC/ZnO. The endpoint of the thermal decomposition temperature also increased from 341 °C for PBC to 374 °C for PBC/ZnO. By comparing different PBC composites, it was found that the thermal decomposition temperature of PBC/MgO is comparable to that of pure PBC. The maximum thermal decomposition temperatures of PBC/SiO_2, PBC/Al_2O_3, and PBC/ZnO increased to more than 340 °C, which was higher than the thermal decomposition end temperature of pure PBC. The thermal decomposition endpoints of PBC/TiO_2 and PBC/ZnO increased to more than 370 °C. In addition, all the PBC composites showed a one-step degradation process, which was proven by the existence of a single peak in the DTA curve.[22–24]

Isothermal Kinetic Analysis of PBC and Its Composites

Isothermal crystallization kinetics can be used to study the crystallinity of crystal nucleation and the crystal growth rate of polycarbonate materials simply and intuitively, which is helpful for further guidance in polymer processing. According to the literature,[13] the isothermal crystallization kinetics of polycarbonate at different temperatures show that the crystallization process of the polymer can be divided into two stages: nucleation and crystal growth. The lower the temperature, the faster is the nucleation rate. The higher the temperature, the faster is the crystal growth rate; that is, the crystallization rate is determined by

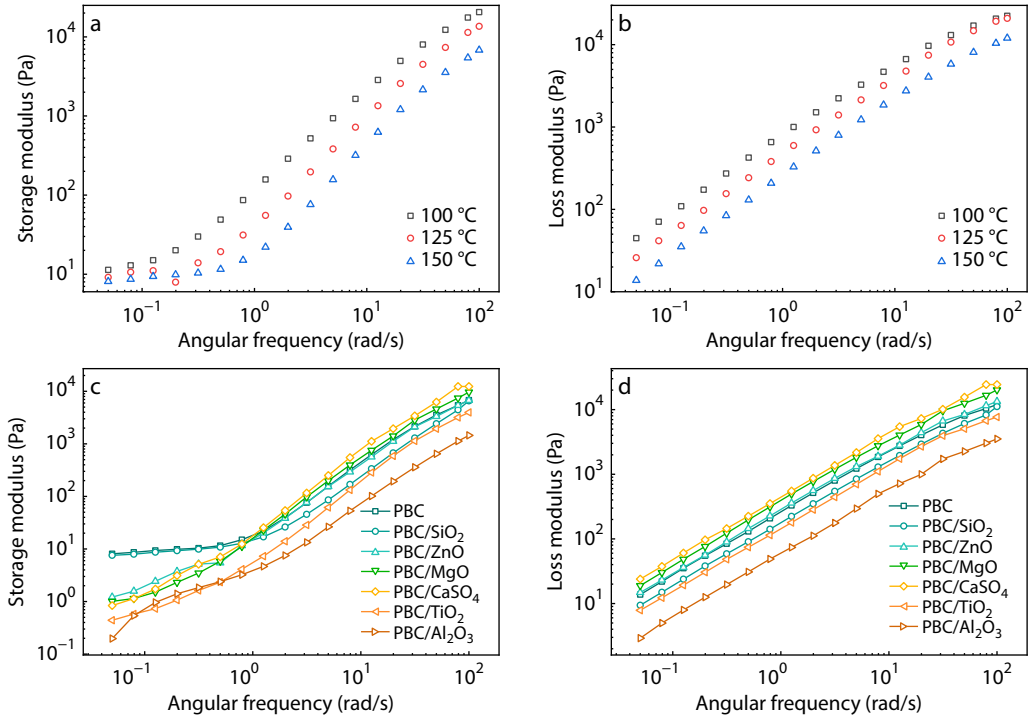

Fig. 2 The frequency dependence of the storage modulus (a) and loss modulus (b) of PBC at three different temperatures of 100, 125 and 150 °C; Frequency dependence of the storage modulus (c) and loss modulus (d) of PBC composite materials at 150 °C.

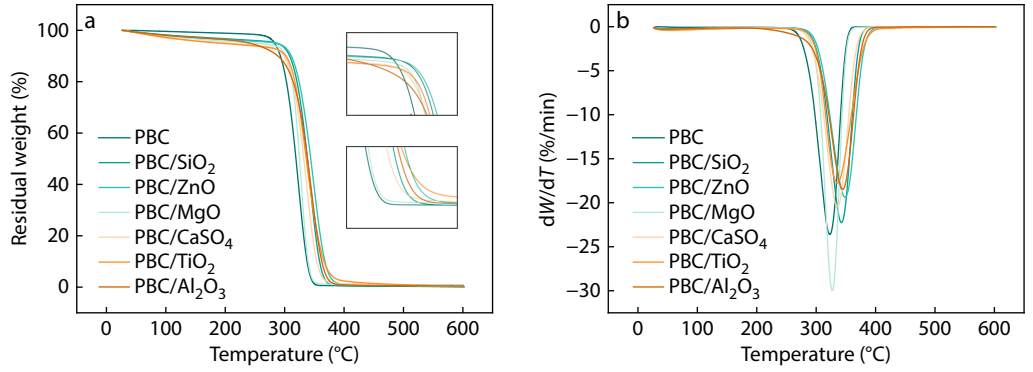

Fig. 3 (a) TG and (b) DTA curves of different PBC composites.

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the nucleation and crystal growth rates. Among them, PBC had the fastest crystallization rate at 10 °C, and the crystallization temperature of this experiment was 10 °C.

To study the effect of inorganic nucleating agents on the crystallization rate and nucleation mode of polycarbonate, the isothermal crystallization kinetics of the composites were analyzed using DSC. The relationship curve between the enthalpy released by isothermal crystallization of the modified PBC composite at 10 °C is shown in Fig. 4. From the diagram, it can be seen that after adding inorganic particles as nucleating agents, the crystallization rate of PBC increased to varying degrees. The shorter the crystallization time of the composite system, the faster the crystallization rate of the system. To study the isothermal crystallization kinetics of PBC and its composites, the relative crystallinity was calculated using Eq. (1).

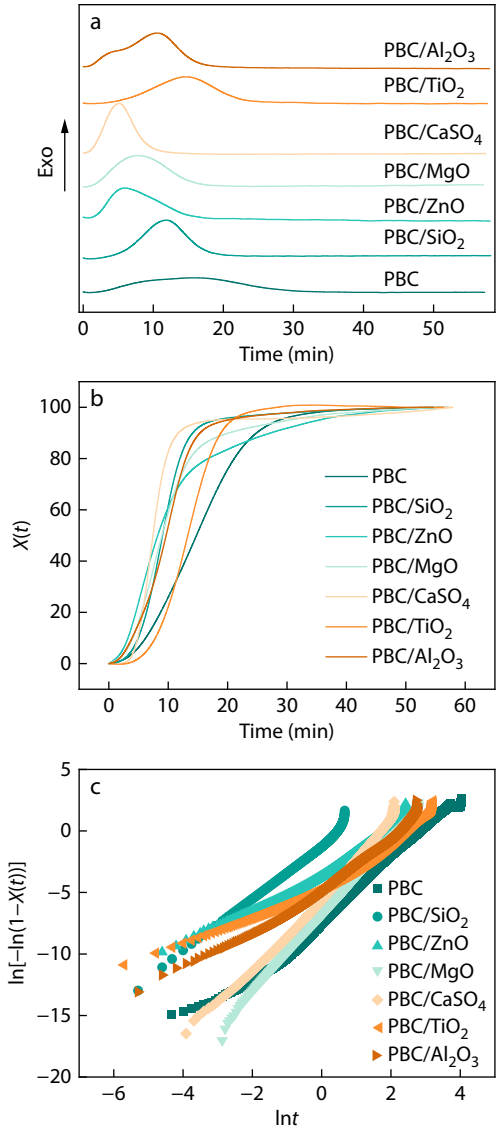

Fig. 4 (a) The relationship curve between the cold crystallization enthalpy and time of PBC during isothermal crystallization at 10 °C; (b) The change curve of relative crystallinity of PBC composites with time during isothermal crystallization at 10 °C; (c) The change of relative crystallinity of PBC composites with time during isothermal crystallization at 10 °C.

$$X(t) = \frac{Q(t)}{Q(\infty)} = \frac{X_c(t)}{X_c(\infty)} = \frac{\int_0^t \left(\frac{dH}{dt}\right) dt}{\int_0^\infty \left(\frac{dH}{dt}\right) dt} \quad (1)$$

where dH represents the crystallization enthalpy measured within the time interval dt, $Q(t)$ is the heat generated at time t, $Q(\infty)$ is the total heat generated by the final crystallization process, t_0 is the initial crystallization time, and t_t and t_∞ represent the time experienced during the crystallization process and after the completion of crystallization, respectively. After the integral calculation, the curve of the relative crystallinity of the PBC composites with time during the isothermal process was obtained. The results are shown in Fig. 4(b). The half-crystallization time ($t_{1/2}$) obtained from the curve of the relative crystallinity with time is listed in Table S2 (in ESI). It can be seen from the table that the half-crystallization time of neat PBC at 10 °C isothermal crystallization is as long as 14.75 min. After adding the nucleating agent, the half-crystallization time was improved. Among these, the PBC/$CaSO_4$ composite exhibited the shortest half-crystallization time. The $t_{1/2}$ values across composites increased in the order: PBC/$CaSO_4$ < PBC/TiO_2 < PBC/MgO < PBC/ZnO < PBC/SiO_2 < PBC/Al_2O_3 < neet PBC. In order to better study the isothermal crystallization kinetics, crystallization rate and nucleation mode of PBC and its composites, the typical Avrami equation (Eq. 2) was used.

$$X(t) = 1 - \exp(-Kt^n) \quad (2)$$

Eq. (3) is often written in a double logarithmic form as follows:

$$\ln[-\ln(1 - X(t))] = \ln K + n\ln t \quad (3)$$

This equation is mainly used to evaluate the Avrami parameter, where n is the Avrami index reflecting the crystallization mechanism, t is the time, and K is the kinetic rate constant involving the crystal growth and nucleation parameters of the molten pool. In general, for different crystallization mechanisms, n should be an integer between 1 and 4. The Avrami parameters n = 1,2 and 3 represent one-dimensional, two-dimensional and three-dimensional crystal growth, respectively. However, the Aravmi index n is not a simple integer and may involve other complex factors, including irregular boundaries of spherulites and/or the composition of diffusion-controlled growth. Fig. 4(c) shows the relationship curves between ln[−ln(1−$X(t)$)] and ln$t$ during isothermal crystallization of the PBC composites at 10 °C. The Avrami exponent n and crystallization rate constant K obtained from the relationship curve of ln[− ln(1−$X(t)$)] and ln$t$ are listed in Table S2 (in ESI). The results showed that the relationship between ln[− ln(1−$X(t)$)] and ln$t$ was linear in the early stage of crystallization for all PBC materials. Compared with the PBC homopolymer, the crystallization rate constant and crystallization rate of the PBC composites were improved.[25]

Dynamic Mechanical Analysis

Dynamic mechanical analysis is an effective method for evaluating the viscoelasticity and interfacial interactions of polymeric materials. By measuring the change in the storage modulus with temperature, the enhancement effect of different inorgan-

ic fillers on the rigidity and thermomechanical properties of polymer matrix composites can be further explored. Fig. 5 shows the temperature dependence of storage modulus and tanδ of neat PBC and its composites.

As shown in Fig. 5(a), the storage modulus of the PBC composites is higher than that of neat PBC over the entire test range, which proves that the introduction of an inorganic nucleating agent improves the mechanical properties of the material. In the low-temperature region, the storage modulus of PBC and its composites was higher than that of neat PBC (1.0×10^3 MPa), indicating that the addition of inorganic nucleating agents had different degrees of constraint on the movement of molecular chains in the glassy state. With an increase in the test temperature, the movement ability of the molecular chain was enhanced, and the storage modulus of the material was gradually reduced, especially in the glass transition region. The storage modulus decreases sharply, but the nucleating agent binds the movement of the molecular chain; thus, the storage modulus of the PBC composite material is still higher than that of pure PBC in the rubber state platform. It can be seen from Fig. 5(b) that all the relatively neat PBC tanδ peaks of the PBC composites move to high temperatures, indicating that the glass transition temperature of the PBC composites increases, which again proves that the addition of a nucleating agent makes the movement of the PBC molecular chain difficult, thus improving the heat resistance of the material. Similar results were obtained by using DSC. For the PBC composites, the increase in the glass transition temperature of PBC/MgO is lower than those of the other composites, and the enhancement effect is relatively weak. This may be due to the poor interfacial compatibility between the nanoparticles and PBC matrix, which leads to stress concentration points and fails to give full play to its enhancement potential. At a similar glass transition temperature, the tanδ peaks from high to low are PBC/ZnO, PBC/TiO_2, PBC/$CaSO_4$, PBC/SiO_2, and PBC/Al_2O_3. The broadening and decrease of tanδ peaks indicate that the internal molecular motion environment of PBC composites is not uniform, the motion unit is smaller, and the distribution is more dispersed. Similar phenomena and conclusions have also been reported for PBC and PLA blends.[10]

DSC

To study the thermodynamic behavior of the PBC composites using different modification methods, the results of the first heating curves of the polymer are shown in Fig. 6, and the corresponding thermodynamic behavior data are summarized in Table S2 (in ESI). The results show that the T_g and T_m of the PBC composites are slightly higher than those of neat PBC, especially for PBC composites without any treatment. The addition of a nucleating agent provides crystallization sites, which promote the crystallization ability of polymer molecular chains and affect the molecular chain movement of polymers. The T_m of the modified polymer, particularly after isothermal annealing, was significantly improved.

The crystallinity of PBC composites was calculated according to the formula $X_{c\text{-}DSC} = \frac{\Delta H_m}{\Delta H_m^0} \times 100\%$, where ΔH_m^0 is the melting enthalpy of 100% crystalline PBC with a value of 137.1 J/g,[23] which can be compared to the crystallinity of PBC composites,[24] and the results are shown in Fig. 6. The crystallinity of PBC composites was significantly higher than that of neat PBC, and the crystallinity of PBC/Al_2O_3 increased to 35.04%. After pre-stretching and isothermal annealing, the crystallinity of the PBC composites improved to varying degrees. Among them, the crystallinity of the polymer after isothermal crystallization showed the most obvious improvement. Thermal annealing increased the crystallinity of PBC/SiO_2 and PBC/ZnO by about 25% and 45%, respectively, compared to those unannealed samples. Conversely, for PBC/Al_2O_3, annealing reduced the crystallinity to a level below that observed in the unannealed state. This may be due to the fact that the crystals that have been well crystallized in the pre-stretching process are broken under the action of unidirectional tension and transformed into multiple tiny and imperfect crystals. However, excessively broken crystals inhibit crystal growth, thereby reducing the crystallinity of the material.

Mechanical Properties

The mechanical properties of aliphatic polycarbonates are closely related to their chemical composition, aggregation structure, morphology, and crystallinity. The mechanical properties of different PBC composites and their mechanical properties under different modification conditions were studied using mechanical tensile tests. Fig. 7 shows the stress-strain curves of PBC and its composites at 50 mm/min at room temperature and the related mechanical properties, such as breaking strength,

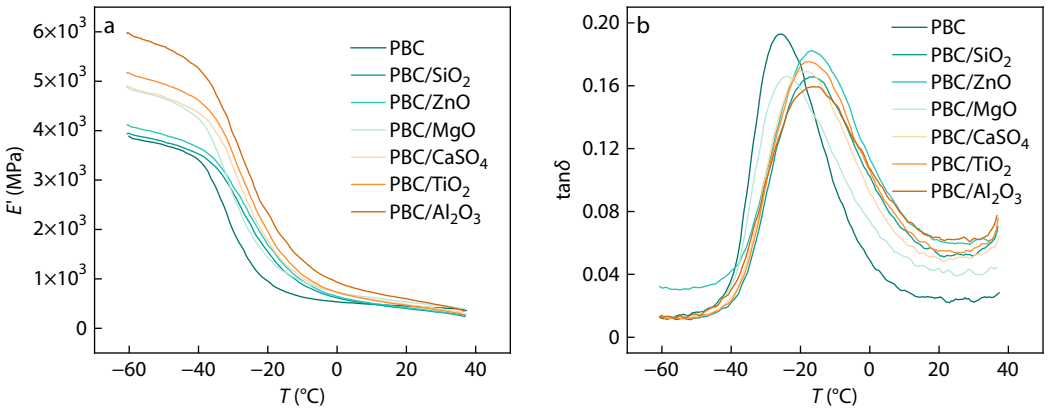

Fig. 5 The performance of PBC in DMA: (a) storage modulus and (b) loss factor.

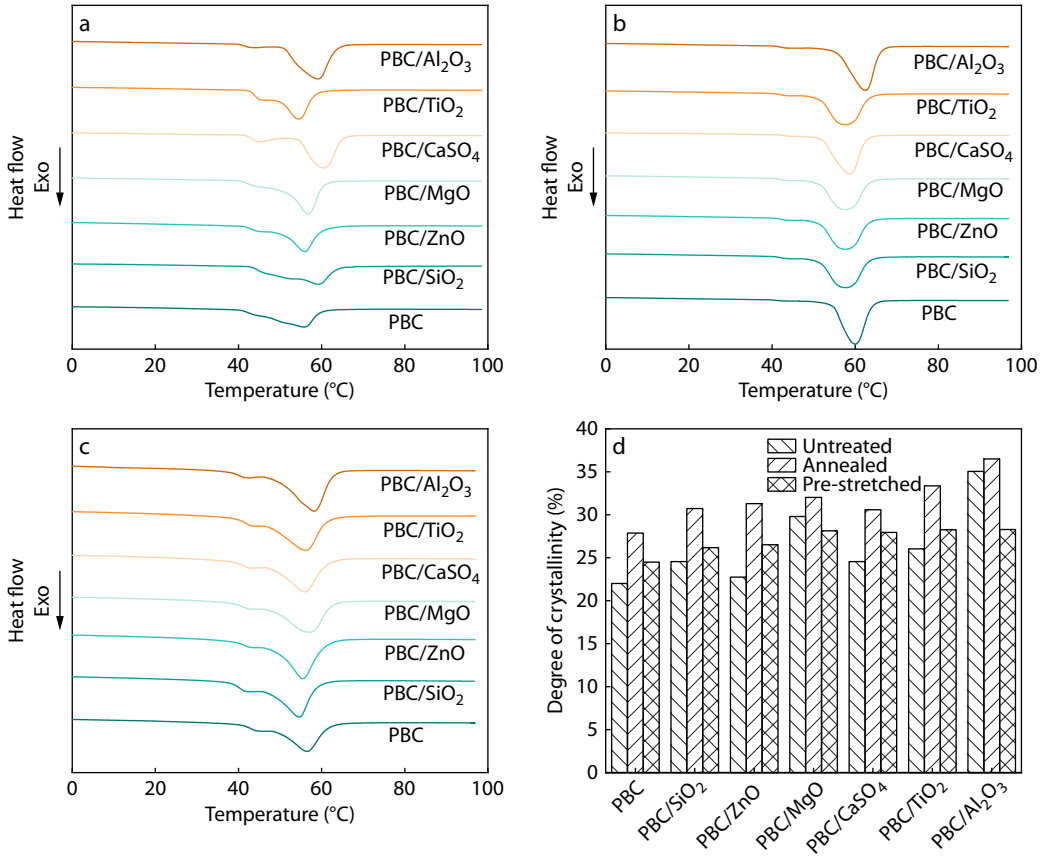

Fig. 6 (a–c) The primary heating curves of PBC composites before and after modification: (a) untreated, (b) isothermal annealed and (c) pre-stretched; (d) Crystallinity of PBC composites under untreated, isothermal annealed and pre-stretched conditions.

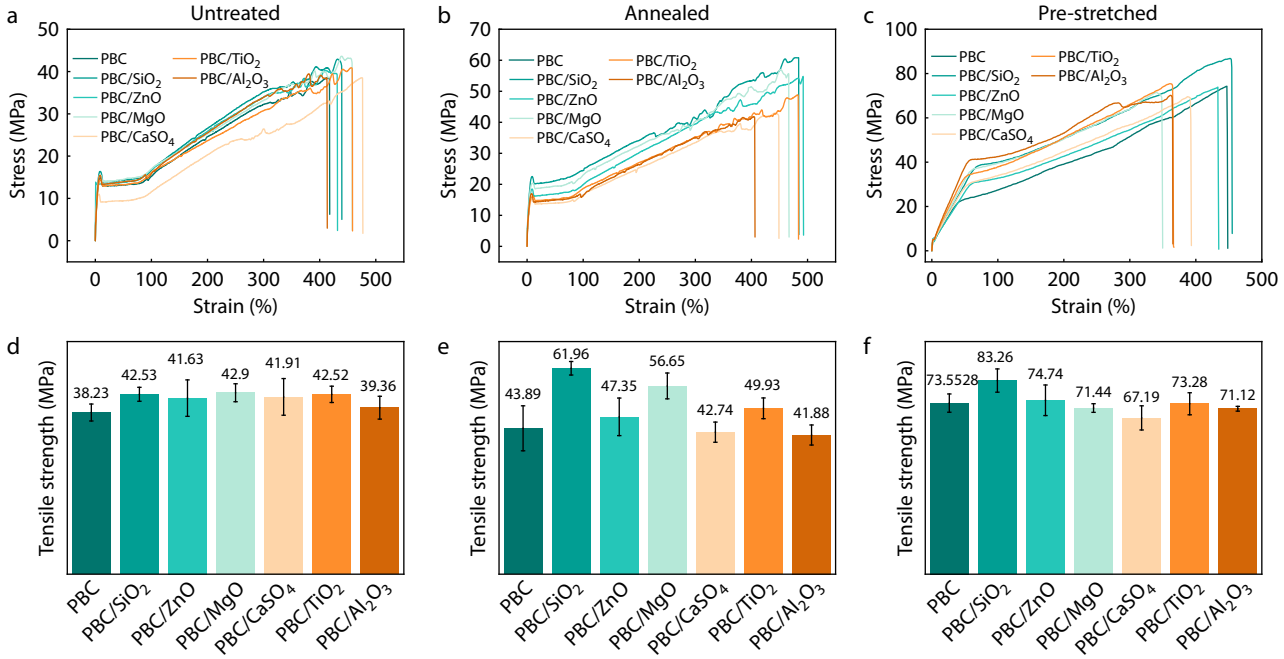

Fig. 7 Stress-strain curves of PBC composites: (a) untreated, (b) annealed and (c) pre-stretched, and tensile strength of PBC composites: (d) untreated, (e) annealed and (f) pre-stretched.

tensile strength, elongation at break, and elastic modulus. The experimental data show that the tensile strength of the pure PBC without modification was (38.23±2.00) MPa, and the elongation at break was 428.27%±28.74%. As shown in Figs. 7(a) and

7(b), the mechanical strength of the PBC composites is higher than that of pure PBC, indicating that the addition of an inorganic nucleating agent helps to improve the tensile properties of PBC, especially PBC/SiO_2 and PBC/MgO composites. The tensile strength of PBC/SiO_2 and PBC/MgO composites reached (42.53±1.65) and (42.90±2.12) MPa, respectively, which increased by 11.24% and 12.22%, respectively. The PBC/Al_2O_3 composite with the smallest increase (39.36±2.69 MPa) was also 1.13 MPa higher than that of pure PBC. However, the elongation at break of the PBC composites did not decrease significantly, especially for the PBC/MgO and PBC/$CaSO_4$ composites. The elongation at break of the PBC/MgO and PBC/$CaSO_4$ composites slightly increased, indicating that this material contributed to the enhancement and toughening of PBC. The elastic modulus and yield strength of the PBC composites exhibited only a small change compared with neat PBC materials. The yield strength of PBC/MgO was the highest (up to 15.49), and the elastic modulus of PBC/SiO_2 was the highest.

The mechanical properties of the PBC composites after isothermal annealing are shown in Figs. 7(c) and 7(d). It can be clearly found that isothermal annealing contributes to the growth of crystals in PBC, and inorganic particles act as nucleating agents to increase the nucleation sites of polymers. The synergistic effect of the two further improves the mechanical properties of the PBC composites. Among them, The tensile strengths of PBC/SiO_2 and PBC/MgO composites increased to (61.96±2.04) and (56.65±3.88) MPa, respectively, which was 62.07% and 48.18% higher than that of blank PBC (unannealed) and 41.17% and 29.07% higher than that of blank PBC (annealed). After annealing, the elongation at break of PBC/SiO_2 composites increased significantly (518%±32%), while the elongation at break of PBC/Al_2O_3 composites after annealing was not as good as that of unannealed PBC composites. There was no significant change in the elongation at break of the other PBC composites, indicating that the elongation at break of most of the composites remained stable after annealing. After annealing, the yield modulus of PBC composites increased by 20%–30% compared to that before annealing, while the elastic modulus remained stable. The tensile properties of the pre-stretched PBC composites (see Figs. 7e and 7f) were significantly improved compared to those of the untreated and isothermally annealed samples. Among them, the tensile properties of pure PBC after pre-stretching were increased to (73.55±3.94) MPa ; the tensile properties of the PBC composites also significantly improved to varying degrees. The tensile properties of PBC/SiO_2 composites have been greatly improved after stretching, and their tensile properties have been improved to (83.26±5.00) MPa, which is 13.20% higher than that of pure PBC after pre-stretching, and their elongation at break was comparable to that of pure PBC. Other PBC composites have different degrees of improvement after pre-stretching, and the order of improvement is: PBC/ZnO > PBC/TiO_2 > PBC/MgO > PBC/Al_2O_3> PBC/$CaSO_4$. The tensile strengths of PBC/Al_2O_3 and PBC/$CaSO_4$ after Pre-stretching is not significantly different from that of neat PBC after pre-stretching, but the elongation at break was significantly reduced, and the yield strength of the PBC composites after pre-stretching was significantly improved compared with that after unannealing and isothermal annealing. Among them, the highest yield strength is that of PBC/MgO (70.97 MPa), which is 3.58 times higher than that of untreated PBC/MgO and 4.81 times higher than that of neat PBC.

The crystallinity and mechanical properties of PBC and its composites under untreated, isothermal annealing, and pre-stretching conditions are shown in Fig. 8. A comprehensive analysis of the relationship between the crystallinity and mechanical properties of PBC and its composites showed that the crystallinity of untreated materials was higher than that of PBC/MgO and PBC/ZnO, but the mechanical properties of the materials were relatively concentrated, indicating that the addition of a nucleating agent can improve the mechanical properties and crystallinity of the materials. In addition, to further investigate the performance changes of the PBC composites after isothermal annealing and pre-stretching modification, the mechanical properties and crystallinity of the PBC/SiO_2 composites were analyzed. It was found that the modified PBC/SiO_2 composites had almost the same crystallization performance as the other materials, and the mechanical properties were significantly improved. On this basis, the optimization of the particle size and content of inorganic nucleating agents will be based on the PBC/SiO_2 composites.

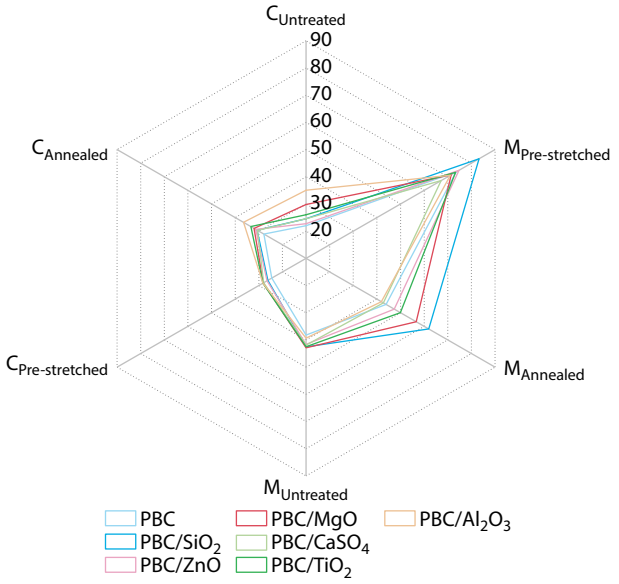

Fig. 8 Comprehensive analysis diagram of the performances of PBC composites.

CONCLUSIONS

This study systematically explored the effects of different inorganic nucleating agents, isothermal annealing, and pre-stretching processes on the crystallization behavior and mechanical properties of PBC. The dispersion and interfacial compatibility of nucleating agents are key factors that influence the properties of PBC. SiO_2 and ZnO were uniformly dispersed within the PBC matrix with good interfacial adhesion, significantly enhancing the storage modulus, crystallization rate, and thermal stability of the material. In contrast, TiO_2 and Al_2O_3 exhibit agglomeration, leading to interfacial defects and limited mechanical enhancement. Isothermal annealing and pre-stretching can synergistically improve the crystallinity and mechanical properties of the PBC composites. Annealing promoted crystal growth, whereas pre-stretching induced crystal orientation. Combined with nu-

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cleating agents, these treatments synergistically increased the tensile strength of PBC/SiO_2 by over 117% compared to the untreated sample, demonstrating a notable synergistic enhancement effect. Crystallinity is positively correlated with mechanical performance. Comprehensive analysis *via* DSC and tensile tests revealed that increased crystallinity was positively associated with improvements in the tensile strength and modulus, particularly under annealing and pre-stretching conditions. The SiO_2 nucleating agent combined with the post-treatment process exhibited the best overall performance. Among the studied systems, PBC/SiO_2 demonstrated superior performance in dispersion homogeneity, crystallization kinetics, thermal resilience, and mechanical reinforcement, facilitating its implementation in film and packaging applications. This study not only elucidates the regulatory mechanisms of nucleating agents and post-processing on PBC properties but also offers a feasible technical pathway for the crystallization modification and high-performance development of polymeric materials. Future work should focus on further optimizing the particle size and content of inorganic nucleating agents based on the PBC/SiO_2 system, expanding its potential applications in flexible electronics, biomedical materials, and other fields.

Conflict of Interests

The authors declare no interest conflict.

Electronic Supplementary Information

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Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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Graphical Abstract

Effects of Different Nucleating Agents, Annealing and Pre-stretching Process on the Crystallinity and Mechanical Properties of Poly(butylene carbonate)

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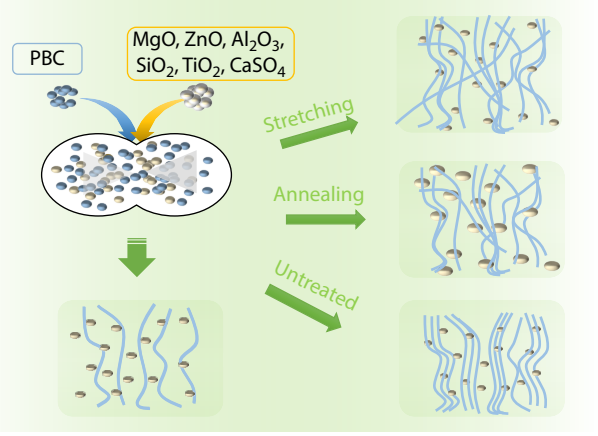
Nucleating agents enhance poly(butylene carbonate) (PBC) performance with annealing and stretching, improving crystallinity and mechanical properties. PBC/SiO_2 strength rose to 61.96 MPa (annealed) and 83.26 MPa (stretched), though agent dispersion varies.



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