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ORIGINAL PAPER

Effect of melt vibration on structure and mechanical properties of HDPE/nano-CaCO$_3$ blend

**Xue-qin Gao · Cong Deng · Jing Xu ·
Zhong-ming Li · Jie Zhang · Kai-zhi Shen**

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Abstract Melt vibration technology was used to prepare injection sample of HDPE/nano-CaCO$_3$ blend, whose mechanical properties were improved significantly. Compared with conventional injection molding, the enhancements of the tensile strength and impact strength of the sample molded by vibration injection molding were 41.2 and 43.2%, respectively. According to the SEM, WAXD, and DSC measurement, it was found that a much better dispersion of nano-CaCO$_3$ in sample was achieved by vibration injection molding. Moreover, crystal orientation degree of matrix HDPE increased under the effect of melt vibration. The crystallinity degree of HDPE in vibration sample increased by 5.5% compared with conventional one. The improvement of mechanical properties of HDPE/nano-CaCO$_3$ blend prepared by low-frequency vibration injection molding attributes to the even distribution of nano-CaCO$_3$ particles and the orientation of HDPE crystals and increase of crystallinity degree under the influence of melt vibration.

Keywords Melt vibration · HDPE/nano-CaCO$_3$ blend · Mechanical properties · Structure

Introduction

For polymer/inorganic nanophase composite, the dispersion of inorganic nanoparticles in polymer is the key to obtain composite with high performance. Whether nano-particles can be dispersed evenly in matrix polymer depends on many factors: specific surface area, surface free energy, surface polarity of nano-particles, surface polarity of polymer, strength of polymer melt, mutual chemical action between

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X. Gao · C. Deng · J. Xu · Z. Li · J. Zhang · K. Shen (✉)
College of Polymer Science and Engineering, State Key Laboratory of Polymer Materials Engineering, Sichuan University, Chengdu 610065, China
e-mail: gxqsnow@163.com

nano-particles and matrix polymer. In addition, the dispersion of nanoparticles is also affected by processing equipment. Presently, the processing methods to make nano-particles disperse homogeneously are wet grinding, melt high-speed mixture, ultrasonic dispersion, etc. [1].

In the work reported in this article, melt vibration technology was used to improve the dispersion of nano-$CaCO_3$ particles in HDPE. As we know, the melt vibration can influence melt rheological properties and enhance the physical properties of molded articles [2, 3]. From the previous study, we know that melt vibration can improve mechanical properties of HDPE due to change of its internal microstructure [4, 5]. However, the research about HDPE/nano-$CaCO_3$ blend by melt vibration has not been studied. Some researchers have worked on modified HDPE by filling it with nano-$CaCO_3$ particles to enhance the strength and toughness of HDPE [6–9]. The studies showed that putting some nano-$CaCO_3$ particles with or without surface treating in HDPE can enhance both the strength and toughness of HDPE to some extent. Nano-$CaCO_3$ particles are easy to agglomerate owing to their high surface energy. The surface treating agent, such as silane, titanium ester, aluminum ester coupling agent, etc., all can accelerate the dispersion of nano-$CaCO_3$ particles in matrix HDPE. The aim of the work reported here was to make use of melt vibration to further improve the dispersion of nano-$CaCO_3$ particles and change morphology of matrix HDPE. Finally, HDPE/nano-$CaCO_3$ composite with high performance will be obtained.

Experimental

Materials

The materials used were HDPE (6100M, Qilu Petrochemical Corporation, China) with a melt flow rate of 0.42 g (10 min^{-1}) measured at 190 °C under 2.16 kg, and nano-$CaCO_3$ (treated by silane coupling agent) with an average grain diameter of 50–70 nm.

Sample preparation

Nano-$CaCO_3$ treated by silane coupling agent was first dried at 80 °C for 4 h in a baking oven in order to remove adsorbed moisture. Then, HDPE/nano-$CaCO_3$ with a mass ratio of 10:1 was pelletized using a twin-screw extruder. Granules obtained were dried at 80 °C for 4 h in a baking oven before they were put into the experimental device. A schematic of the experimental device is shown in Fig. 1a. Granules obtained were put into a polymer plasticizing system. Homogenous melt plasticized by this system was delivered into the melt chamber, whose temperature was kept at 210 °C. The vibration and injection ram could be driven by an injection and vibration system. It was used not only to carry out melt vibration, but also to realize injection molding. When the vibration system did not operate, the experimental device was equivalent to a conventional injection molding machine. Otherwise, when the vibration system and injection system both operated, this

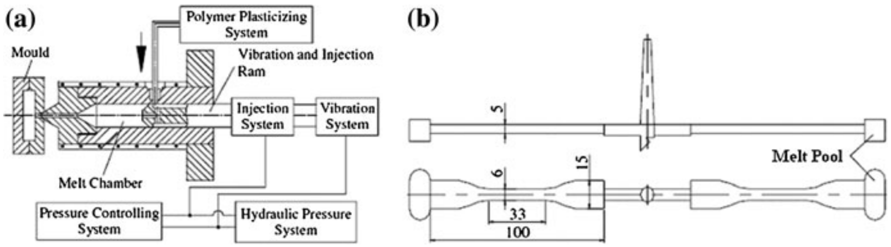


Fig. 1 Schematic diagram of experimental devices: **a** vibration injection molding; **b** the layout of dumbbell specimens in the mold with main dimensions (mm)

experimental device could implement vibration injection molding. The vibration system was driven by a hydraulic pressure component. When the vibration system operated, the vibration and injection ram could oscillate at certain frequencies and pressures. The oscillation of vibration and injection ram made the melt in the melt chamber vibrate in the process of injection molding. During the course of vibration injection molding, the vibration pressure amplitude (0–80 MPa) was superimposed on the base injection pressure (40 MPa). The other main processing parameter was vibration frequency (0.5 Hz). The temperature and pressure of the melt in the melt chamber could be monitored at any time. A sample mold was set up on the experimental device. The temperature of the mold was 20 °C in the experiment. The layout of sample with main dimensions is shown in Fig. 1b. The melt pool is like an elastic spring to induce compression and expansion of melt in the runner of this experimental device.

Tensile testing

Dumbbell specimens were obtained after cutting off gates of moldings and the molten pool. The main dimensions of dumbbell specimen are shown in Fig. 1b. These dumbbell specimens obtained at various processing conditions were used as tensile specimens. A universal electronic testing machine (Instron 4302) was used for tensile testing at room temperature (23 °C), at a crosshead speed of 50 mm min^{-1}.

Impact testing

Bars (6 × 5 × 33 mm) as impact specimens were obtained after cutting off the dumbbell part of the tensile specimens. The impact specimens were V-type notched using a cutter (XQZ-1). An Izod impact machine (UJ-40) was used to measure the impact strength of sample at room temperature.

SEM measurements

SEM measurements were conducted using a Hitachi model X-650 instrument. Brittle fracture samples were obtained after freezing using liquid nitrogen. The brittle fracture surfaces were sputtered with a thin layer gold before the SEM analysis.

Wide-angle X-ray diffraction (WAXD) measurements

WAXD experiments were conducted using a Rigaku D/MAX-A diffractometer. Cu K_α radiation was used for X-ray diffractometry. The 10 × 10 × 1 mm samples were sliced from the shear layer (1.5 mm from the surface layer) of the static and dynamic injection moldings, respectively, parallel to the flow direction (MD). The planes for measurement were ground and polished prior to being measured.

DSC measurements

DSC tests were conducted using a Perkin-Elmer TA2000 differential scanning calorimeter, which scanned at 10 °C min^{-1}. The sample for DSC measurements was taken out from the shear layer of the molding. The weight of sample each testing was 5 mg. During the measurement, dried nitrogen gas was purged at a constant flow rate.

Results and discussion

Mechanical properties

Figure 2 shows changes of tensile strength of HDPE and HDPE/nano-$CaCO_3$ blend with pressure amplitude. The data points where pressure amplitude is zero represent the tensile strength of conventional sample. The tensile strength of HDPE/nano-$CaCO_3$ blend is greater than that of neat HDPE for both conventional and vibration samples. This shows that silane coupling agent makes the nano-$CaCO_3$ particles bind well with HDPE. Nano-$CaCO_3$ particles have played a reinforcement role for conventional injection molding. Tensile strengths of HDPE and HDPE/nano-$CaCO_3$ blend all increase obviously with increase of pressure amplitude. When pressure amplitude is maximal (80 MPa), tensile strength of HDPE is 41.2 MPa, a 37.9% increase compared with the conventional strength (29.9 MPa), and tensile strength of HDPE/nano-$CaCO_3$ blend is 45.4 MPa, a 41.2% increase compared with the conventional strength (32.2 MPa). It can be seen that the increase of tensile strength of HDPE/nano-$CaCO_3$ blend is higher than that of neat HDPE using melt vibration. This might be because the melt vibration allows a more even dispersion of nano-$CaCO_3$ particles within HDPE/nano-$CaCO_3$ blend as well as inducing an orientation of HDPE molecular chains. The evenly dispersed nano-$CaCO_3$ particles can act as nucleating agents in HDPE/nano-$CaCO_3$ blend. They make HDPE crystallize in a way of heterogeneous nucleation. Thus, the crystallinity of vibration samples will be enhanced. The enhancement of crystallinity is in favor of the increase of tensile strength of HDPE/nano-$CaCO_3$ blend. Moreover, melt vibration can disperse nano-$CaCO_3$ particles so well as to reduce the mechanical weak spots caused by agglomerated particles.

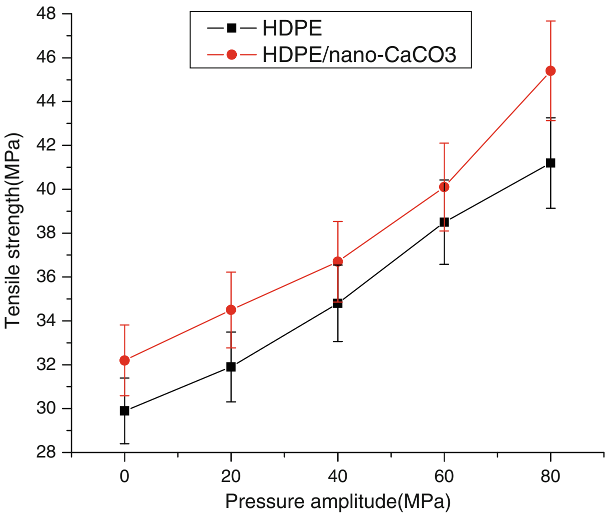


Fig. 2 Changes of tensile strength of HDPE and HDPE/nano-$CaCO_3$ blend with pressure amplitude

Figure 3 shows changes of impact strength of HDPE and HDPE/nano-$CaCO_3$ blend with pressure amplitude. Impact strengths of HDPE and HDPE/nano-$CaCO_3$ blend all increase notably with increase of pressure amplitude. The larger the pressure amplitude, the higher the impact strength is. When pressure amplitude is maximal (80 MPa), impact strength of HDPE is 61.7 kJ/m^2, a 46.1% increase compared with the conventional strength (42.2 kJ/m^2), and impact strength of HDPE/nano-$CaCO_3$ blend is 66.5 kJ/m^2, a 43.2% increase compared with the conventional strength (46.4 kJ/m^2).

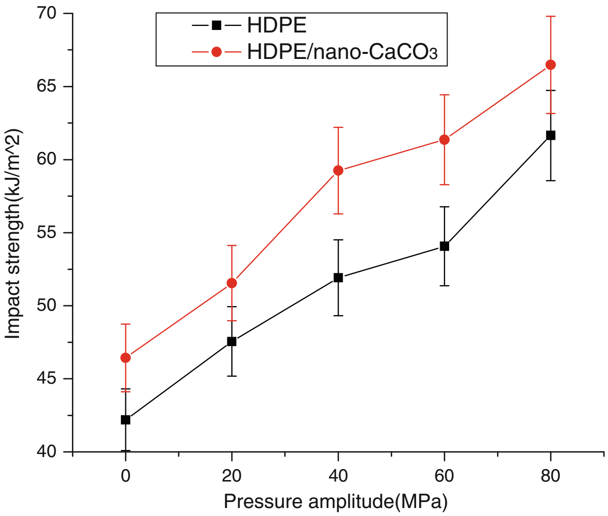


Fig. 3 Changes of impact strength of HDPE and HDPE/nano-$CaCO_3$ blend with pressure amplitude

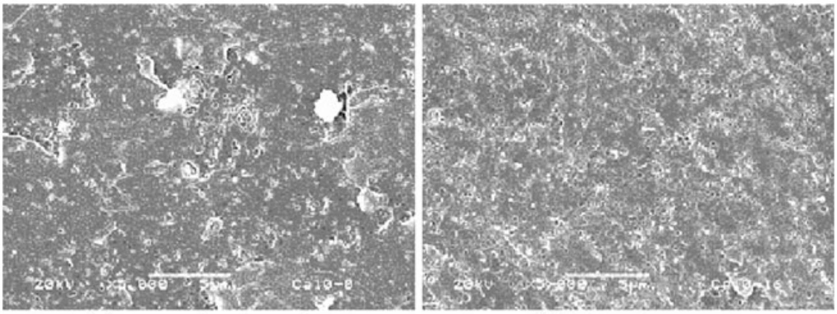
The previous study of our team shows that melt vibration can make spherulite of HDPE diminish [10]. The decrescent spherulite can improve the toughness of HDPE. This is the reason for the enhancement of neat HDPE impact strength. For HDPE/nano-$CaCO_3$ blend, the nano-$CaCO_3$ particles can toughen the blend. The toughening mechanism of $CaCO_3$ is that during impact, surface debonding between $CaCO_3$ and HDPE matrix occurred, which released strain constraint on the HDPE matrix and therefore allowed its large plastic deformation. Moreover, when sample is impacted, nano-$CaCO_3$ particles as stress concentration points can induce HDPE matrix to produce plentiful craze-shear ribbons which consume some impact energy. Thus, the impact strength of HDPE/nano-$CaCO_3$ blend is higher than that of neat HDPE for both conventional and vibration injection moldings. For HDPE/nano-$CaCO_3$ blend, melt vibration allows a more even dispersion of nano-$CaCO_3$ particles as well as inducing a change of HDPE crystal morphology. The increase of impact strength of HDPE/nano-$CaCO_3$ blend is the compositive result of evenly dispersed nano-$CaCO_3$ particles and change of matrix HDPE morphology. The even dispersion nano-$CaCO_3$ particles can induce HDPE matrix to produce more craze-shear ribbons which consume more impact energy. Thus, the even dispersion nano-$CaCO_3$ particles is in favor of enhancement of impact strength. For matrix HDPE, the decrescent spherulite can improve the toughness. However, the enhancement of crystallinity makes against impact strength. On the whole, the influence of disadvantages is smaller than that of advantages. Therefore, melt vibration still can improve the impact strength of HDPE/nano-$CaCO_3$ blend notably.

The larger the pressure amplitude, the stronger the effect of vibration field is. Therefore, the impact strength and tensile strength of samples are highest at the maximal pressure amplitude of 80 MPa.

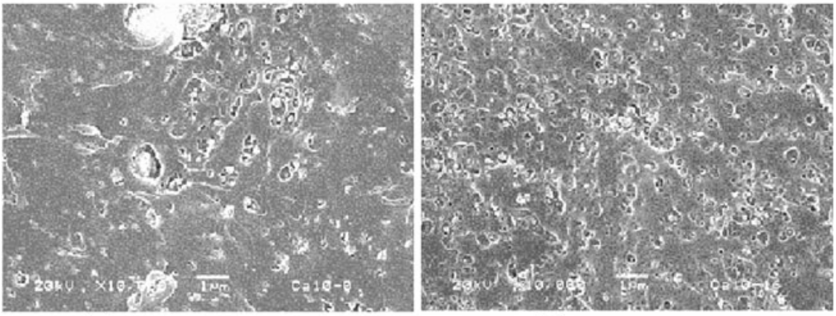
SEM analysis

Figure 4 shows SEM micrographs of brittle fracture surfaces of the conventional and vibration samples for HDPE/nano-$CaCO_3$ blend. The magnification of Fig. 4a and b is 5000×, and that of Fig. 4c and d is 10,000×. Figure 4a and c shows SEM micrographs of conventional samples, and Fig. 4b and d shows SEM micrographs of vibration samples.

It can be seen that there are many agglomerated nano-$CaCO_3$ particles in conventional samples. These agglomerated particles can cause stress concentration and become weak spots of material mechanical properties. However, nano-$CaCO_3$ particles disperse much better in the vibration samples obtained at pressure amplitude of 80 MPa. This also validates the foregoing conjecture about the reason for impact strength and tensile strength improvement of samples obtained by melt vibration. In addition, there are some cavities on the conventional and vibration brittle fracture surfaces. For the conventional samples, the cavities produced by interface stripping are large because of agglomeration of nano-$CaCO_3$ particles. From Fig. 4, it can be seen that the cavities of conventional samples are obviously larger than those of vibration samples. Melt vibration can make nano-$CaCO_3$ particles disperse homogenously. The cavities of vibration samples became notably



(a) Conventional sample **(b)** Vibration sample



(c) Conventional sample **(d)** Vibration sample

Fig. 4 SEM micrographs of conventional and vibration brittle fracture samples

smaller. This makes the defective area of vibration samples reduce greatly [6]. Thus, the strength of vibration samples is higher than that of conventional samples.

WAXD analysis

Figure 5 shows WAXD curves of conventional and vibration samples at shear layers for HDPE/nano-$CaCO_3$ blend. It can be seen that there are two strong diffraction peaks at $2\theta = 21.5^\circ$ and 23.9°. They are diffraction peaks of (110) and (200) crystal planes of HDPE, respectively [11, 12]. The peak height ratio of (200) and (110) can be used to characterize the change of crystal orientation degree of HDPE matrix [13]. For HDPE/nano-$CaCO_3$ blend, the peak height ratio is 0.256 for conventional sample and 0.368 for vibration sample. The peak height ratio of vibration sample is larger than that of conventional sample. This shows that HDPE crystal orientation degree of vibration sample increases compared with that of conventional sample. Orientation of HDPE crystals can make tensile strength of vibration sample enhance effectively.

DSC analysis

DSC analysis can be used to obtain the enthalpy of fusion of HDPE in HDPE/nano-$CaCO_3$ blend. The crystallinity of sample can be calculated by the following equation:

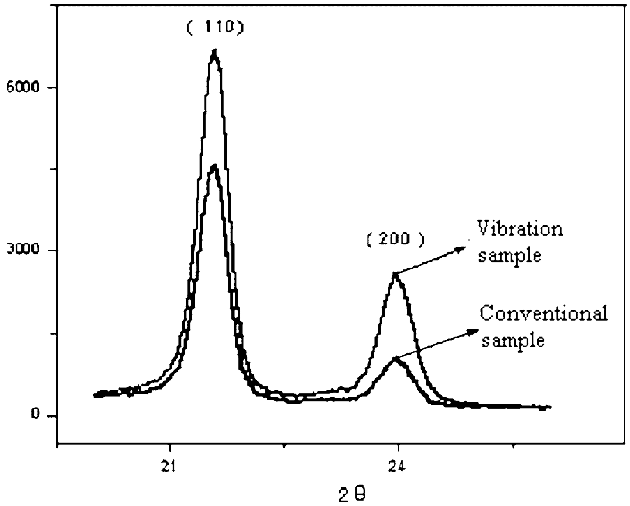


Fig. 5 WAXD curves of conventional and vibration samples at shear layers

$$X_c = \left\{\Delta H_C / \left[(1 - \Phi)\Delta H_m^0\right]\right\} \times 100\%,$$

where X_c is the crystallinity of sample, ΔH_C is the measured enthalpy of fusion of sample from DSC thermogram, Φ is the mass fraction of nano-$CaCO_3$ in sample, ΔH_m^0 is a perfect enthalpy of fusion of HDPE (293 J g^{-1}) [14].

The temperatures of melting peaks for HDPE/nano-$CaCO_3$ sample prepared under the conventional and vibration conditions and calculated crystallinity values are shown in Table 1. The melting peak of vibration sample obtained at the pressure amplitude of 80 MPa is a little higher than that of conventional sample. Moreover, the melting end temperature of vibration sample also moves to higher temperature a little. This indicates that vibration sample contains more thick lamellae of HDPE compared with conventional sample [15].

An evident increase in enthalpy of fusion in vibration sample can be found compared with conventional sample. Therefore, the crystallinity of vibration sample increases by 5.5% compared with conventional sample. This might be because that melt vibration makes matrix HDPE molecular chains arrange orderly. The increase of order of molecular chains will make HDPE crystallize easier. On the other hand, melt vibration improves the dispersion of nano-$CaCO_3$ in HDPE/nano-$CaCO_3$ blend. Nano-$CaCO_3$ particles acting as nucleating agent make HDPE crystallize in a way of heterogeneous nucleation. Thus, the crystallinity of vibration sample is higher than that of conventional sample.

Table 1 DSC results obtained for conventional and vibration samples

Samples	Melting peak (°)	ΔH_C (J g^{-1})	Crystallinity (%)
Conventional sample	132.3	163	61.2
Vibration sample	133.1	178	66.7

Conclusions

The conclusions of this work can be summarized as follows.

(1) Melt vibration technology can improve the mechanical properties of HDPE/nano-$CaCO_3$ sample significantly. Compared with conventional injection molding, the enhancements of the tensile strength and impact strength of the sample molded by vibration injection molding were 41.2 and 43.2%, respectively.
(2) Melt vibration can allow more even dispersion of nano-$CaCO_3$ particles within HDPE/nano-$CaCO_3$ vibration sample. The agglomerated particles are broken up and dispersed homogenously by melt vibration. This is one of the main reasons for the improvements of impact strength and tensile strength of HDPE/nano-$CaCO_3$ vibration sample.
(3) Crystal orientation degree of matrix HDPE increases under the effect of melt vibration. The crystallinity degree of vibration sample increases by 5.5% compared with conventional sample. Orientation of HDPE molecular chains and increase of crystallinity degree are all favorable to the improvement of tensile strength of HDPE/nano-$CaCO_3$ vibration sample. The crystal (molecular) orientation of matrix HDPE is a very important affecting factor to increase both tensile and impact strength measured in the flow direction (MD) effectively.
(4) Microscopic structure and morphology obtained by SEM, WAXD, and DSC analyses provide powerful evidence for explaining the reason for improvement of macroscopic mechanical properties of HDPE/nano-$CaCO_3$ blend by melt vibration. The improvement of mechanical properties of HDPE/nano-$CaCO_3$ blend prepared by low-frequency vibration injection molding attributes to the even distribution of nano-$CaCO_3$ particles and the orientation of HDPE crystals and the increase of crystallinity degree under the influence of melt vibration.

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