

Thermal Properties of HDPE/CaCO₃ Materials

Zou Yiyi, Wang Kejian*, Wang Xuewei, Li Sihan and Low Zihao

College of Mechanical and Electrical Engineering, Beijing University of Chemical Technology, Beijing,100029, China

Abstract

The melting crystallization process of HDPE composite filled with $CaCO_3$ powder was characterized by DSC. The results show that compared with HDPE and other HDPE composites with calcium carbonate ratio, when the content of $CaCO_3$ is 30%, the crystallization entropy and melting entropy of HDPE are lower, the crystallinity is decreased, the melting point is slightly increased, the melting peak area is smaller, and the extrusion injection molding will be more energy saving.

Keywords: High density polyethylene; Inorganic particle packing; Thermal property

Introduction

Cheap inorganic materials are widely used as fillers in the plastics industry to improve the mechanical and thermal properties of polymers [1-3]. In particular, composites made from HDPE and calcium carbonate powder are widely used in films, large containers, logistics pallets, and drainage pipes. This paper studies the melting crystallization characteristics of HDPE/CaCO₃ composites and reveals that adding calcium carbonate to HDPE composites can improve the thermal stability of materials, reduce the production cost of HDPE plastic products, and reduce the melting enthalpy during the production and processing of HDPE. This may mean that the addition of calcium carbonate is able to reduce the consumption of power resources during processing.

Experimental

Materials

High Density Polyethylene (HDPE), DMDA Type, 8007 (Shenhua Baotou Coal Chemical Co., LTD., China); A nearly spherical particle calcium carbonate powder with a maximum diameter of $0.1 \mu m$ (Shandong Zhongtian Mining Co., LTD., China).

Composite material preparation

The $CaCO_3$ and deionized water were mixed and stirred in the ratio of 1:1. Stand for 12h, filter out the water, and put the precipitated $CaCO_3$ in the oven for drying at 100 °C. High density polyethylene and dried calcium carbonate were evenly mixed in a high-speed mixer according to the mass ratio of 9:1, 8:2 and 7:3. The composite materials were added to the extruder to squeeze, and then the composite materials were cut and granulated. The finished granules were dried at 60 °C for 12h, and the samples were made for the determination of thermal properties.

Measurements

5-10mg samples were taken from the prepared composite materials and placed in a ceramic crucible. The crystallization behavior and melting characteristics of composites at 20 °C to 180 °C were studied by DSC-200F3, a German galloping scanning calorimeter, at the heating and cooling rates of 10K/min in nitrogen atmosphere.





*Corresponding author: Wang Kejian, College of Mechanical and Electrical Engineering, Beijing University of Chemical Technology, Beijing,100029, China

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Results and Discussion

Curves (a) and (b) in (Figure 1) are DSC curves during the second temperature rise and temperature drop of the material. The curves show that HDPE and the HDPE material with $CaCO_3$ added have only one melting peak and crystallization peak ,the melting point slightly increases with the increase of $CaCO_3$ content, and the area of melting peak and crystallization peak decreases with the increase of $CaCO_3$ content. The decrease of melting peak means that the consumption of power resources can be reduced in the injection molding or extrusion process. The crystallization peak shifts towards high temperature with the increase of $CaCO_3$ content. The melting and crystallization behavior of materials is further

analyzed, and the melting enthalpy, crystallization enthalpy and crystallinity in the second heating and cooling process are drawn in Table 1. With the increase of $CaCO_3$ content, crystallization enthalpy and crystallinity will decrease, mainly because $CaCO_3$ occupies the space of HDPE macromolecules during the cooling crystallization process, which restricts the movement of macromolecular chains [4]. The limitation degree of macromolecular conformation in the crystallization process can be described by crystallization entropy, according to the formula:

$$\Delta S_c = \Delta H_c / T_c \tag{1}$$

 $\Delta H_{_c}$ is crystallization enthalpy and $T_{_c}$ is crystallization temperature.

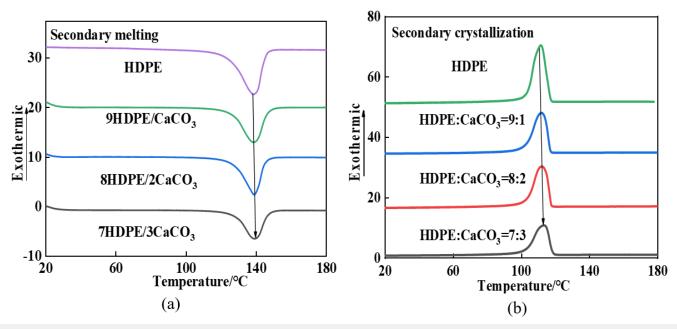


Figure 1: DSC curves of the HDPE/CaCO₃ composite at the second cooling and the second melting. **Table 1:** Dsc characteristics of HDPE/CaCO₃ composites.

Sample	Melting Temperature (°C)	Enthalpy of Melting (J/g)	Crystallization Temperature (°C)	Enthalpy of Crystallization (J/g)	Degree of Crystallinity (%)
HDPE:CaCO ₃ =7:3	138.6	152.91	113.3	152.76	75.5
HDPE:CaCO ₃ =8:2	138.3	195.65	112.3	180.4	77
HDPE:CaCO ₃ =9:1	137.3	203.4	111.8	200.6	77.1
HDPE	137.1	229.27	111.7	228.3	78.9

In the melting process, the enthalpy and entropy of melting decreased with the increase of $CaCO_3$ content, indicating that the conformation of HDPE macromolecule is also limited during the melting process. It can be seen from (Figure 2) that crystallization entropy decreases with the increase of calcium carbonate content. Therefore, the greater the amount of calcium carbonate in the

composite, the greater the reduction of macromolecular freedom in the crystallization process. The melting entropy decreases with the increase of calcium carbonate content. Therefore, the greater the content of calcium carbonate, the greater the reduction of macromolecular freedom in the smelting process, the higher the thermal stability of the composite.

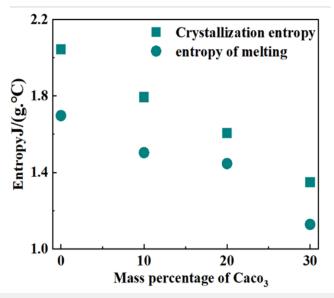


Figure 2: Crystallization entropy and melting entropy of HDPE composites with different calcium carbonate contents.

Conclusion

- a. When $CaCO_3$ is added to HDPE, the HDPE material with 30% $CaCO_3$ content can reduce the consumption of power resources. The heat insulation capacity of $CaCO_3$ particles improves the heating capacity of the material, but the crystallinity of the material decreases.
- b. The melting peak area of HDPE composite can be reduced by DSC with more CaCO₃ added.
- c. Fusion entropy and crystallization entropy can be used to quantitatively compare the conformation restriction degree of HDPE macromolecules in the melting and crystallization processes of composites with different contents of CaCO₃.

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