

A study on thermal behaviour of HDPE/CaCO₃ nanocomposites

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Materials

ABSTRACT

Purpose: In order to improve physical and mechanical properties of high density polyethylene (HDPE) addition of filler, rigid particles and even elastomer to HDPE is very common. One of the most important filler which is added to it is nano size calcium carbonate (CaCO₃). To avoid agglomeration of nano size calcium carbonate addition of fatty acids such as stearic acid is very common.

Design/methodology/approach: In the current study, nanocomposites with 10vol% nano size calcium carbonate were prepared. To investigate the role of stearic acid on nanocomposite behaviour, nanoparticles were coated at different stearic acid content. Thermal behaviour of high density polyethylene and its nanocomposites reinforced with both uncoated and coated calcium carbonate were investigated. For this purpose differential scanning calorimetry (DSC) test was used.

Findings: The results of DSC test showed that addition of 10vol% calcium carbonate to HDPE causes a slightly rise in its melting point but stearic acid content has no significant effect on the melting temperature of HDPE nanocomposites.

Research limitations/implications: : Agglomeration of nanosized calcium carbonate during sample preparation was the major research limitation.

Originality/value: Crystallization temperature of HDPE with addition of 10vol% calcium carbonate increases, while addition of stearic acid causes to decrease it. Both stearic acid content and 10vol% calcium carbonate have no significant effect on crystallinity index of HDPE.

Keywords: Composite; HDPE; CaCO₃; Thermal behaviour

1. Introduction

High density polyethylene (HDPE) is a linear polyethylene (PE) with density 0.94-0.97 g/cm³, molecular weight 50,000-250,000 and high crystallinity. It is produced by co-or homo polymerization in slurry or gas phase at relatively low pressure and temperature. HDPE has excellent low temperature toughness, chemical resistance, good dielectric properties and relatively high softening temperatures but poor weatherability [1].

In order to reduce cost or enhance physical and mechanical properties of HDPE, some additives can be added to it. Fillers and reinforcement used include talc, calcium carbonate (CaCO₃), mica, wollastonite, glass fibre, glass bead, jute, etc. [1,2].

Calcium carbonate is one of the most abundant minerals in the earth's crust. Precipitated Calcium Carbonate (PCC) can be produced in all three crystal modifications of CaCO₃ and a wide variety of particle sizes and shapes, including plates and acicular forms. For filler applications the particles have an ultimate particles size of 50-100 nanometers, a specific surface area of 15-25 m²g⁻¹

and a low aspect ratio. Surface treated grades are coated with lipophilic substances such as stearic acid (SA) or calcium stearate to improve dispersibility, increase oxidation resistance of the filled resin, and reduce wear on processing machinery [1-3].

It is clear that the calcium carbonate can change the physical and mechanical properties of high density polyethylene, because of its nature, size, shape and distribution [3-15]. This study is focused on the effect of surfactant content on the crystallization and melting behaviour of HDPE/CaCO₃ nanocomposites.

2. Experimental procedure

In order to investigate the effect of surfactant on thermal behaviour of HDPE/CaCO₃ nanocomposites HDPE granules and precipitated calcium carbonate powders which are produced by Solvay company were prepared. The average particle of PCC was about 65 nm. size of particles Table 1 illustrates specification of HDPE and calcium carbonate powders.

Table 1.
Specifications of PCC powders

Material	grade	Particle size (nm)	Coupling agent Content (Wt%)
HDPE	Injection	-----	-----
CaCO ₃	PCC	68	0
CaCO ₃	PCC	72	2
CaCO ₃	PCC	62	3
CaCO ₃	PCC	62	3.8
CaCO ₃	PCC	69	4.5

Oven-dry PCC powders and HDPE pellets were first mechanically mixed to achieve HDPE/10vol% CaCO₃ nanocomposites. The mixtures were then fed into a two stage processing unit composed by a twin screw non-intermeshing corotating mixer (COMACPLAST, Milano) and a MV45 single-screw extruder (COMACPLAST, Milano) with 45 mm diameter, length/diameter ratio 28:1 and were extruded. Unfilled HDPE was also similarly processed as a control. The extruded material was cooled in water at room temperature. The resultant nanocomposite pellets were then granulated by a milling device.

In order to investigate the thermal properties of pure high density polyethylene and its nanocomposites, calorimetric analysis was carried out. A Perkin-Elmer differential scanning calorimetry DSC-2C calorimeter was used to analyze the samples. The temperature calibration of DSC was obtained by measuring the melting temperature of Indium. All measurement were performed under nitrogen flow. The mass of the samples used varied between 5 to 9 mg. The samples were put in an aluminum crucible and crimped using a small press.

For getting information about thermal properties, the bellow temperature program was followed. During the first heating run, which was performed at rate of 10°C/min, the temperature range examined was from room temperature to the melting point of the samples. After reaching this temperature, the specimens were then cooled at the same rate of 10°C/min. A second heating run was performed at 10°C/min. Using the above temperature program the following information can be achieved:

T_m: The melting temperature of polymer, corresponding to the maximum of the melting peak in the thermogram.

ΔH_m: Heat of melting, the amount of energy which is consumed for melting and corresponding area in the thermogram.

T_c: The crystallization temperature, corresponding to the minimum of the crystallization peak in the thermogram.

ΔH_c: Heat of crystallization, the amount of energy which evolved during crystallization measured from the corresponding area in the thermogram.

Temperatures and heat of melting (crystallization) were determined from the peak maximum (minimum) and the corresponding area in the thermogram, respectively.

The percentage of crystallinity of HDPE and its nanocomposites are calculated as:

$$X_c(\text{HDPE}) = \Delta H^*(\text{HDPE}) / \Delta H^0(\text{HDPE}) \quad (1)$$

$$X_c(\text{Nanocomposite}) = \Delta H^*(\text{Nanocomposite}) / \Delta H^0(\text{HDPE}) \quad (2)$$

where ΔH*(HDPE) is the apparent enthalpy of fusion per gram of HDPE in the nanocomposite, ΔH⁰(HDPE) is the heat of fusion of 100% crystallinity HDPE, taken as 70 cal/g from what proposed by Wunderlich [3] and ΔH*(Nanocomposite) is the apparent enthalpy of fusion per gram of nanocomposite. The relationship between ΔH*(Nanocomposite) and ΔH*(HDPE), X_c(HDPE) and X_c(Nanocomposite) can be achieved by the following equations (3) and (4) respectively.

$$\Delta H^*(\text{HDPE}) = \Delta H^*(\text{Nanocomposite}) / W(\text{HDPE}) \quad (3)$$

$$X_c(\text{HDPE}) = X_c(\text{Nanocomposite}) / W(\text{HDPE}) \quad (4)$$

where the W(HDPE) is the weight fraction of HDPE in the nanocomposites.

3. Results and discussion

The results of DSC thermogram of pure HDPE and its nanocomposites are summarized in Figures (1) to (5). For comparison the results of DSC test of pure HDPE are shown with square symbol in all Figures.

Figure (1) shows the effect of the stearic acid on the melting point of first and second heating run (T_{mI} and T_{mII}) of nanocomposites. As it is seen, addition of 10vol% PCC to HDPE causes a slightly rise in both T_{mI} and T_{mII}, but it seems that an increase in stearic acid has no significant effect on the melting temperature of HDPE. In fact, the little fluctuation of melting temperature observed, as the amount of stearic acid increases, is within the typical experimental accuracy for this type of measurements. Figure (2) illustrates the variation of ΔH_{mI} and ΔH_{mII} per gram of nanocomposites as a function of stearic acid content. Indeed the addition of 10vol% PCC to HDPE causes to decrease the melting heats during the first and second heating run of the nanocomposites. This reduction of heat of melting can be mainly accounted for by dilution effect due to substitution of some HDPE by CaCO₃ [9,10].

A better comparison can be obtained by using the enthalpy of fusion per gram of HDPE in the nanocomposite, calculated by means of equation (3). The results are shown in Figure (3) which displays the dependency of the heat of fusion per gram of HDPE versus stearic acid content. As it is clear from this figure, during both first and second heating runs, the melting enthalpy is practically constant and it seems that the stearic acid has no significant effect on the heat of melting of neat HDPE.

Figure (4) shows the result of crystallization behaviour of HDPE/10vol% PCC with respect to stearic acid content. An

increase in crystallization temperature (T_c) clearly would indicate that crystallization started earlier in the filled nanocomposites than in the unfilled HDPE.

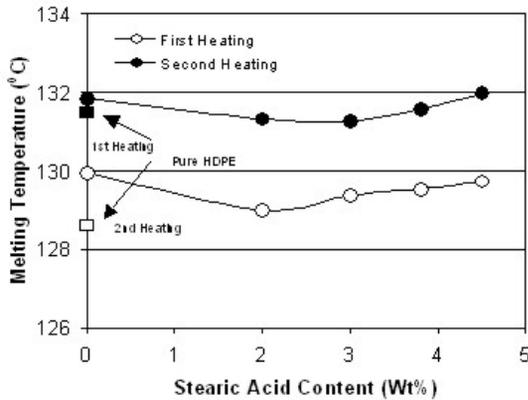


Fig. 1. Variation of melting temperature of HDPE nanocomposites versus stearic acid content

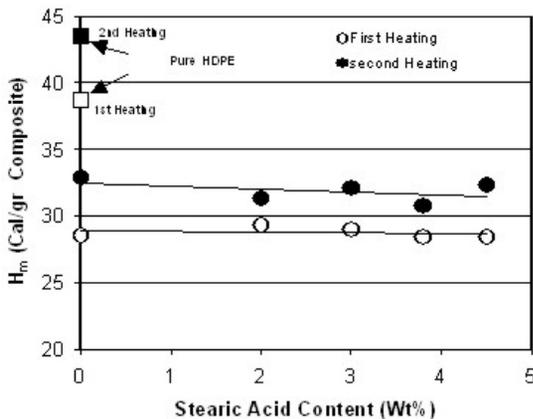


Fig. 2. Variation of heat of fusion of HDPE/10vol%CaCO₃ nanocomposites versus stearic acid content (per gram nanocomposite)

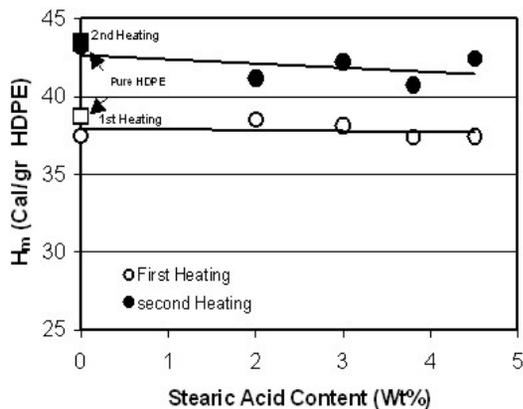


Fig. 3. Variation of heat of fusion of HDPE nanocomposites versus stearic acid content (per gram HDPE)

The question here is whether nanosizes CaCO₃ (with or without surfactant) in this system acts as a nucleating agent, promoting the crystallization process. While the crystallization temperature is almost unaffected. For nanocomposites with coated PCC, this increase is less marked (about 5°C) and appears quite clearly that the stearic acid coated filler particles have very little influence on the crystallization behaviour of HDPE/10vol% CaCO₃ nanocomposites.

In fact addition of stearic acid seems to compensate the effect of CaCO₃. This is can be easily explained by the fact that when the surface of CaCO₃ is coated by stearic acid, which is chemically very similar to polyethylene, the interactions between the filler and the matrix dramatically decreases and the particles cannot play any role as nucleating agents [4].

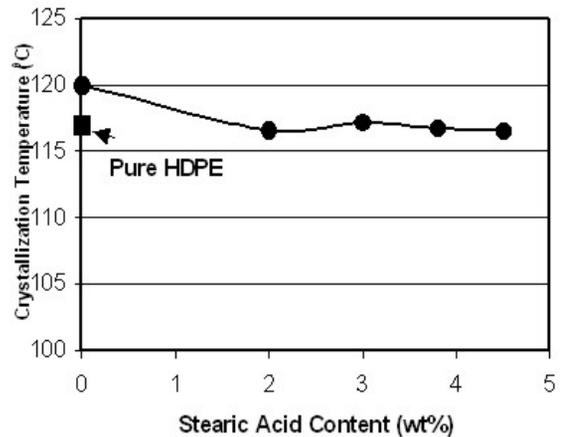


Fig. 4. Dependency of crystallization temperature of HDPE nanocomposites on stearic acid content

Figure (5) shows the dependency of crystallinity index of HDPE as a function of stearic acid content. As it is seen, the degree of crystallization of all nanocomposites (X_c (Nanocomposite)) depends on precipitated calcium carbonate content. This is obviously because 10% of the volume in the nanocomposites are occupied by inorganic particles. However, when the crystallinity index is computed in terms of just the amount of high density polyethylene, referred to in Figure (5) as X_c (HDPE), this figure is constant for all nanocomposites and is not very sensitive to stearic acid. The crystallinity index ranges, for all nanocomposites, between 59 and 61.8%, while the corresponding value for high density polyethylene is about 62%.

The above discussion on the nucleating effect of coated and uncoated precipitated calcium carbonate is quite relevant in relation to recent findings by Bartzak et al. [5] on the morphology and orientation of high density polyethylene in sub-micron thickness films grown on precipitated calcium carbonate and crosslinked ethylene-octene rubber substrates. By using combined WAXS measurements and AFM imaging, these authors concluded that, for films of thickness less than 0.3 μm , lamellar crystallites preferentially grow "edge-on", in sheaf-like morphology, on the calcite or rubber interfaces with the (100) crystallographic planes of the lamellae lying parallel to the interfaces, while in films thicker than 0.4 μm , the spherulitic

morphology becomes dominant. This change in morphology and crystalline orientation has been attributed by Bartczak [5] to accelerated secondary nucleation on the layer of lamellae formed adjacent to the substrate, resulting in oriented "edge-on" growth, parallel to this surface.

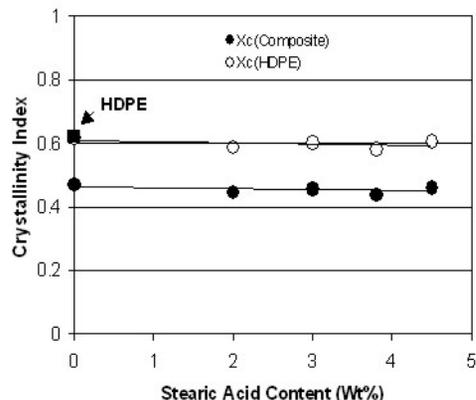


Fig. 5. Variation of crystallinity index of HDPE in HDPE nanocomposites versus stearic acid content

Bartczak et al. [5] suggested that these findings provided strong support for the toughening mechanism proposed by them to explain the particle size effects found by Wu [6] in toughened nylons and other semi-crystalline polymers, also attributed to the so called interparticle distance effect.

4. Conclusions

In order to investigate the role of stearic acid content in crystallisation and thermal behaviour of HDPE nanocomposites, a series of high density polyethylene /10vol% precipitated calcium carbonate nanocomposites with different stearic acid content were prepared. Differential scanning calorimetry (DSC) data are included in this research. The results of DSC tests show that:

- 1) Addition of 10vol% precipitated calcium carbonate to HDPE causes a slightly rise in both T_{mI} and T_{mII} .
- 2) Increasing stearic acid content has no significant effect on the melting temperature of HDPE nanocomposites.
- 3) Addition of 10vol% precipitated calcium carbonate to high density polyethylene causes to decrease heat of fusion of it per gram of nanocomposite and has no great effect on heat of fusion of HDPE per gram of HDPE.
- 4) On increasing the stearic acid content, the heat of fusion of high density polyethylene (both per gram of HDPE and per gram of nanocomposite) did not show particular variation.
- 5) Crystallisation heat of high density polyethylene per gram of nanocomposite decreases while crystallisation heat of HDPE per gram of HDPE did not show any appreciable variations, when 10vol% precipitated calcium carbonate is added to it.
- 6) Stearic acid content and 10vol% calcium carbonate have no significant effect on crystallinity index of HDPE(both per gram of HDPE and per gram of composite)

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