

Role of Surface Active Agent on Dimensional Stability of HDPE/CaCO₃ Nanocomposites

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ABSTRACT: Dimensional stability is normally defined as the ability of a material to maintain its size and shape under various temperatures and stresses. The parameter, which is used to determine dimensional stability, is thermal expansion coefficient. This work deals with the study of the dimensional stability and thermal stability of high-density polyethylene (HDPE) and its nanocomposites by the presence of different stearic acid (SA) content as a modifier of surface. To investigate the role of surfactant on dimensional stability of HDPE nanocomposite reinforced with nano-sized calcium carbonate (CaCO₃), nano-sized calcium carbonates were coated with different SA content. Standard specimens of HDPE/10 vol% CaCO₃ nanocomposite were performed using injection method. To study dimensional stability of HDPE/10 vol% nanocomposites, dilatometry method was used. The results showed that addition of nano-sized CaCO₃ caused the decrease of thermal expansion coefficient of HDPE. In addition, dimensional stability of HDPE/10 vol% CaCO₃ improved due to increasing SA content. Also, addition of inorganic fillers and surfactant retarded the thermal oxidation of HDPE.

KEY WORDS: nanocomposite, HDPE, surface-active agent, stearic acid, nano-sized calcium carbonate, thermal expansion, dimensional stability, thermal degradation.

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Figures 5–7 appear in color online <http://jtc.sagepub.com>

INTRODUCTION

HIGH-DENSITY POLYETHYLENE (HDPE) is one of the most important thermoplastic polymers. Low cost, easy production by almost all convenient procedures such as injection, compression, and blow molding, besides high toughness especially at low temperature, good chemical, and electrical resistivity, makes HDPE the first choice for many consumers. Nevertheless, low melting point and poor thermal properties limited its application in industry. To improve the mechanical and physical properties and for promotion of service temperature of HDPE, addition of secondary particles such as talc, mica, and calcium carbonate (CaCO_3) to it is suggested [1–6].

Among the above fillers, CaCO_3 with 85% of total consumer filler is the most preferred. The CaCO_3 can change the physical and mechanical properties of HDPE because of its nature, size, shape, and distribution [7–11]. The performance of CaCO_3 depends on particle size and its distribution as well as its interface with matrix [12–14]. The results of previous works showed that the mechanical and physical properties of HDPE/ CaCO_3 composites enhanced as particle size of CaCO_3 decreased. This is because there is an inverse relationship between debonding stress and particle size [15,16] and theoretically, if the particle size approaches zero, debonding between CaCO_3 and HDPE cannot occur [16]. However, probability of agglomeration of particles increases as particle size decreases. With regards to the above, using very small particle will be constrained. Furthermore, agglomeration of nano-sized particles hinders the easy production of nanocomposites because of high interaction force between nanoparticles as the size lessened.

Also, to avoid agglomeration and to reduce the surface energy of nano-sized particles, surface treatment of particles using fatty acids, especially stearic acid (SA) is commonly used [17–20].

According to literature survey, there are a few studies that points out on the role of SA on physical and mechanical properties of HDPE/ CaCO_3 nanocomposites [12,13,21–23]. For example, Lazzeri et al. [13] showed that addition of coated nano-sized CaCO_3 could compensate decreasing of the tensile properties compared to the uncoated precipitate CaCO_3 . The results of their study illustrated that addition of fatty acids such as SA or other fatty acid can be a good way to make uniform dispersion with suitable adhesion between particle and matrix [13,21]. Also, according to that reported by Sahebian et al. [21], addition of nano-sized CaCO_3 to HDPE causes a drastic effect on stress-whitening zone appearing in front of precrack during fracture toughness test [21]. Thermal behavior of HDPE/ CaCO_3 nanocomposites was investigated by Zebarjad et al. [23].

They reported that nano-sized CaCO₃ has a significant effect on crystallinity, melting point, and heat of melting of HDPE, and addition of SA content cannot change the mentioned parameters [23]. Kwon et al. showed that the tensile stress and complex melt viscosity of the calcite-filled polyethylene (PE) composites were higher than that of unfilled ones [14].

The low thermal stability of PE is a great problem throughout PE processing and usage. Thermal degradation studies of polymers are necessary as many applications depend on their thermal stability.

Some published works represent the promotion of thermal degradation of PE when mineral filler added to it [24,25]; also, in recent years, nanocomposites-based PE have been studied widely due to their significant improvement in thermal properties and mechanical strength at low filler loading [26–32].

The thermal oxidation products and kinetics of PE composites was studied by Yuan et al. [26]. They demonstrated that the inorganic fillers have great effects on the thermal oxidation kinetics i.e., both the activation energy and the preexponent factor increases. This means that the addition of inorganic fillers retards the onset of thermal oxidation of HDPE.

Another important property of composites is the degree of thermal expansion, or how much the material expands with an increase in temperature. It can be measured by thermal expansion coefficient that is unique for different materials. This property plays a critical role in design of electronic packaging used for microelectronic devices. Composites used for the structural components of aircraft or other technological systems that are subjected to extreme environments need a low coefficient of thermal expansion. Though the dimensional stability and thermal stability of HDPE and its nanocomposites are well known, there is no published work concerning these nanocomposites. This study focuses on the effect of both surfactant content and nano-sized CaCO₃ particles on the thermal stability, dimensional stability, and thermal expansion coefficient of HDPE and its nanocomposites.

EXPERIMENTAL PROCEDURE

Sample Preparation

In order to study the effect of surfactant on dimensional stability of HDPE/CaCO₃ nanocomposites, granulated HDPE and nano-sized CaCO₃ from Solvay, Italy, were performed. Table 1 reports the particle size and percentage of surface factor of used material.

Figure 1 shows transmission electron microscope (TEM) micrograph taken from used nanoparticles of CaCO₃. As it can be seen, morphology of used particle is irregular, and the average of particle size is about 70 nm.

Table 1. Specification of nano-sized CaCO_3 particles and HDPE.

Material	Commercial name	Particle size (nm)	Percentage of surface factor (wt%)
HDPE	B4020 N1332	–	–
CaCO_3	SOCAL310	60–70	–
CaCO_3	SOCAL312	60–70	3
CaCO_3	SOCAL314	60–70	4.5

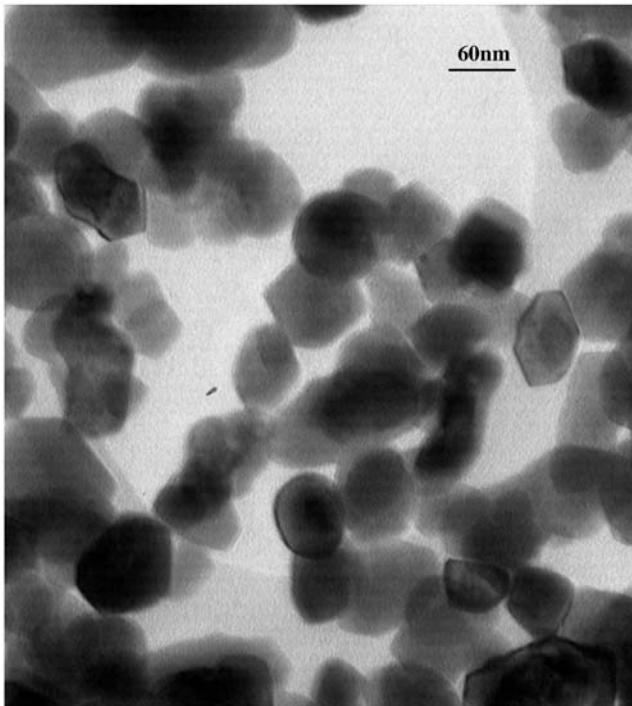


Figure 1. TEM micrographs of nano-sized CaCO_3 .

At the beginning of the process and before mechanical mixing, nano-sized calcium carbonates were dried under vacuum at 80°C for a minimum of 8 h. Dried nano-sized calcium carbonates and granulated HDPE are mixed mechanically to achieve HDPE/10 vol% CaCO_3 nanocomposites. The mixture was extruded through MV45 twin-screw extruder. The speed of extruder was selected as 60 rpm. The temperature was increased progressively along the mandrel from 160°C to 200°C . The standard

Table 2. Specification of produced nanocomposites.

Material	HDPE volume content (%)	Nominal SA/CaCO ₃ weight ratio (g acid/kg CaCO ₃)
Pure HDPE	100	–
C100	90	0
C102	90	20
C104	90	40

specimens were made using injection molding method. The sample sizes were $4 \times 4 \times 18 \text{ mm}^3$. Just for simplicity, the produced nanocomposites were coded as illustrated in Table 2.

To reveal the dispersion of nano-sized CaCO₃ in matrix, the fracture surface of produced nanocomposite was evaluated using scanning electron microscope (SEM).

Dilatometry Test

Dilatometry test is the simplest way to predict dimensional stability of materials. The dilatometry apparatus was Dima_85ECO3080. The machine was equipped with cooling circulation system. The sample was put in the exposed heating zone and was heated at various heating rates, that is, 10, 20, and 40°C/min. The heating was limited between room temperature and 90°C. The change in length corresponding to each temperature was achieved directly. Three samples for each material were tested.

Thermobalance

The thermogravimetric analysis (TGA) was performed with Shimadzu, TGA50 instrument. As for the nonisothermal crystallization kinetics, the samples of about 4 mg were heated upto 700°C at the nominal heating rate of 10°C/min, and continuous records of sample temperature, sample weight, and its first derivative were taken.

At least, three specimens for each type of material were tested by TGA tests, and the average values were reported.

RESULTS

Micrographs from fracture surface of nanocomposites are shown in Figure 2. As seen, there are both nano-sized and some agglomerated particles. In fact, the same authors in another published paper [18] showed

that the average agglomerated size of nano-sized CaCO_3 depends on SA. They showed that the average agglomerated size for C100, C102, and C104 is about 416, 283, and 259, respectively [18].

Figure 3 shows the variation of change in length versus temperature for HDPE and its nanocomposites. For all materials, there is an increase in length change as temperature increases. It can be observed that temperature sensitivity of HDPE decreases in the presence of both coated and uncoated nano-sized CaCO_3 . For example, at 80°C , the length change of pure HDPE is about 0.12 mm, while for C100, C102, and C104 nanocomposites are about 0.095, 0.09, and 0.07 mm, respectively. Also, it is clear that the slope of all curves decreases as SA content of nano-sized CaCO_3 increases. The reason for dependency of dimension of HDPE part on temperature can be attributed to the chain relaxation, and free volume and slip interchain

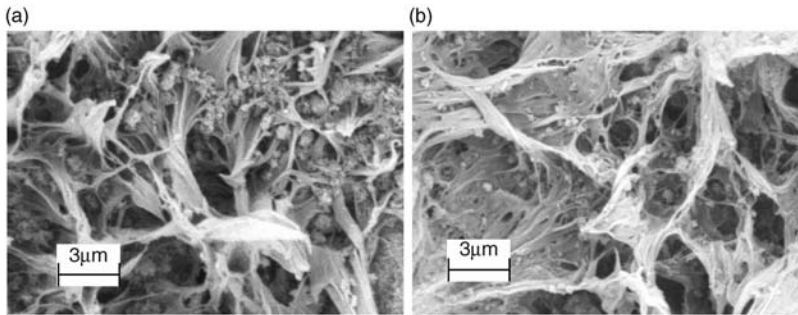


Figure 2. (a,b) SEM micrograph of fracture surface of C104 and C100.

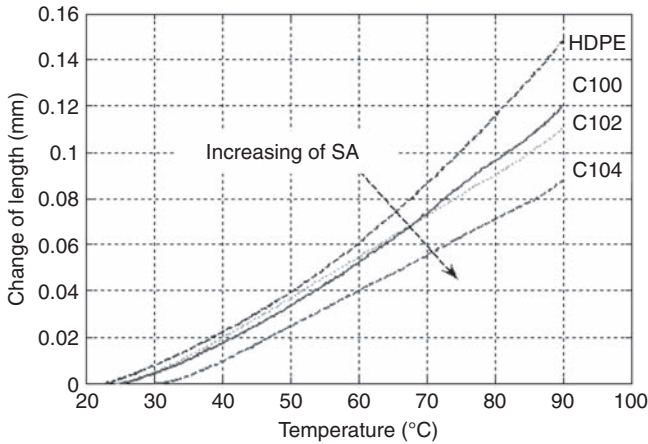


Figure 3. Variation of change of length vs temperature as a function of SA content.

mechanism particularly above glass transition temperature. In fact, the amount of free volume have an inverse relation with dimensional stability of polymers, so one of the reason for higher dimensional stability of nanocomposite with respect to HDPE can be related to decreasing of free volume due to presence of nanofillers.

Besides, the authors believe that the differences between dimensional stability of HDPE and its nanocomposites can be referred to crystallinity index because the free volume of HDPE chains depends on both crystalline and amorphous regions. Lazzeri et al. [13] obtained the crystallinity index of the same material and showed that the crystallinity index of all nanocomposites is almost constant (71–73%), indicating that the SA content on the particles has no influence on the crystallinity of the polymer matrix, while the corresponding value for pure HDPE is about 56% [13]. In fact, addition of SA obliterates the effect of nano-sized CaCO₃. This can be explained by the fact that when the surface of CaCO₃ is coated by SA, which is chemically quite similar to PE, the interactions between the filler surface and the matrix substantially decrease and the particles are not shown to behave as nucleating agents [13].

It seems that the reason for C104 being more dimensionally stable than both C102 and C100 is related to good dispersion of nano-sized CaCO₃ because of the presence of SA. In fact, SA content concentrates on surface of particles to avoid agglomeration of nano-sized CaCO₃ and increases the total surface area [21].

The results of the current study showed that dimensional stability of all materials, including HDPE and its nanocomposite, increases as heating rate increases. Figure 4 illustrates the variation of change in length of C104

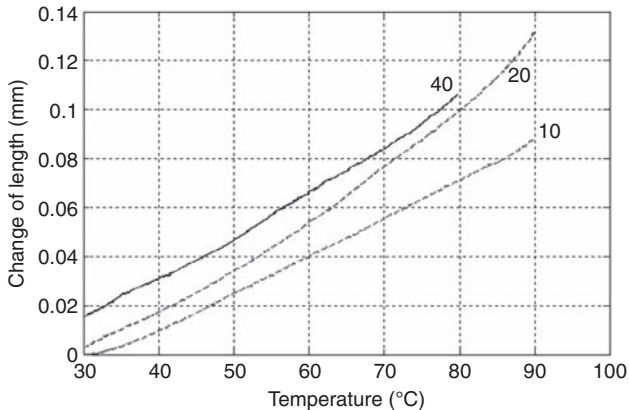


Figure 4. Dependency of change of length of C104 sample on temperature as a function of heating rate.

samples versus temperature as a function of heating rate. The reason for the dependency of dimensional stability of HDPE and its nanocomposite on heating rate can be referred to the fact that heating of whole of the samples needs a specific time, and by increasing heating rate, the surface of sample does not have enough time to transfer heat from one point to another [33,34].

Because of the importance of thermal expansion coefficient compared to change in length, in the current study, dependency of thermal expansion coefficient of HDPE and its nanocomposites on temperature were taken into account. The thermal expansion coefficient at constant pressure can be represented using the following equations:

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P, \quad (1)$$

where α , V , and T are thermal expansion coefficient, specimen volume, and temperature, respectively. Equation (1) can be shown as a function of specimen length in the following form:

$$\alpha = \frac{1}{3L} \left(\frac{\partial L}{\partial T} \right)_P \quad (2)$$

The value of linear thermal expansion of HDPE at different temperature ranges are summarized in Table 3. Since dimensional stability of HDPE is much lower than that of ceramic or even metallic materials, addition of ceramic material such as CaCO_3 can improve it. The interesting result is dependency of thermal expansion coefficient of HDPE/10 vol% CaCO_3 nanocomposites on SA content. Figure 5 illustrates the variation of thermal expansion coefficient of nanocomposites of HDPE versus temperature. Comparison of Table 3 and Figure 5 shows that thermal stability of HDPE improves if coated or uncoated nano-sized CaCO_3 is added to it.

The subject that is still under question is as to why thermal conductivity coefficient can be influenced by SA. In fact, there is a small compatibility between nano-sized CaCO_3 and HDPE because of the large differences between their polarities. Furthermore, the surface energy of nano-sized CaCO_3 is greater and the particles prefer to aggregate together. Addition of SA causes to create a compatible phase between CaCO_3 and HDPE,

Table 3. Thermal expansion coefficient of HDPE.

Temperature (K)	303–333	333–363
Thermal expansion coefficient (1/K)	10.5×10^{-5}	17.3×10^{-5}

reducing surface energy of nanoparticle and leads nano-sized particles to make uniform distribution according to Figure 2. Actually, SA plays like an interlayer and makes chemical bond or mechanical interlocking bond with both filler and polymer, resulting in the improvement of dimensional stability [35]. On the other hand, the presence of SA on surface of nano-sized particles results in more cohesive forces and consequently, more constraint for polymer chains.

Figure 6 shows the value of thermal expansion coefficient of HDPE/10 vol% CaCO₃ as a function of average particle size. As seen, decreasing the particle size leads to the improvement of dimensional stability.

In summary, the main deformation mechanisms of pure HDPE are relaxation chains, increase in free volume, and slip interchain mechanism. By addition of nano-sized CaCO₃ to HDPE, debonding phenomenon will be added to other mechanisms. Since during debonding, volume constancy rule is not valid, one may conclude that debonding mechanism can be a main expansion mechanism. Pukanszky and Voros [16] developed a model to show debonding stress is a function of thermal stress and particle size. Based on their model, the required stress for debonding increases as particle size decreases or thermal stress raises. It is worth noting that increase in the debonding stress leads to the promotion of dimensional stability of the materials.

Figure 7(a) shows the normalized TGA curves obtained at 10°C/min for the pyrolysis and the oxidative degradation of HDPE and HDPE/CaCO₃

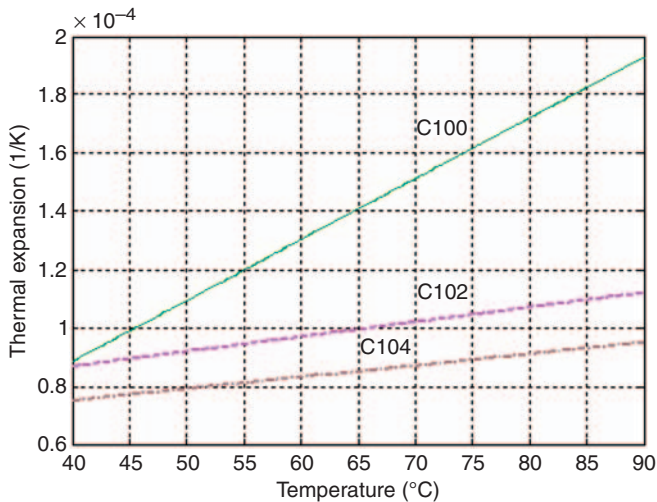


Figure 5. Variation of thermal expansion coefficient of HDPE/CaCO₃ nanocomposites vs temperature as a function of SA content.

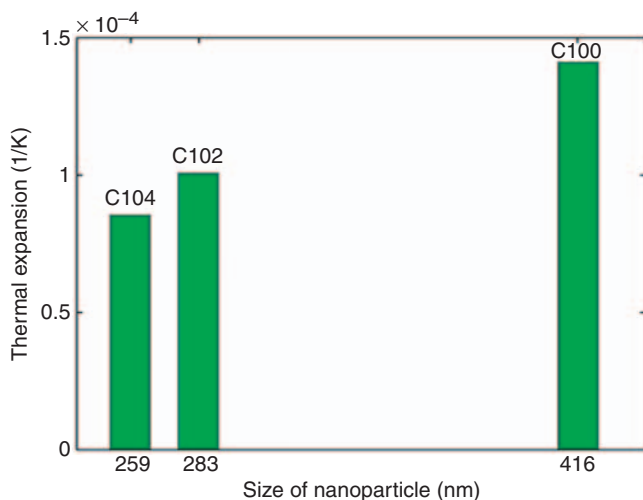


Figure 6. Variation of thermal expansion coefficient of HDPE/CaCO₃ nanocomposite vs particle size as a function of SA content.

nanocomposites, and Figure 7(b) demonstrates the corresponding derivative curves (differential thermogravimetric (DTG) curves). According to Figure 7(a), the lowest thermal stability has been observed for pure HDPE. Also, it is indicated that the presence of CaCO₃ filler and surfactant can improve the thermal stability of nanocomposites. The presence of nano-sized CaCO₃ particle can hinder the flexibility of HDPE chains and increase the crystallinity index. Therefore, thermal degradation of polymer chains occurs at higher temperature with respect to pure HDPE. Zhang et al. [29] shows that strong interaction between CaCO₃ particles and HDPE matrix can restrict the main chain segmental motion and reduce the mobilization of PE chains.

The different polarity of CaCO₃ and HDPE and high surface energy of nanoparticles cause to small compatibility between CaCO₃ and HDPE. So, the lower effect of nano-sized CaCO₃ particles on thermal degradation of C100 sample can be expected. Addition of SA modifies the effect of nano-sized CaCO₃. Good distribution of nano-sized CaCO₃ in HDPE matrix is observed, as shown in Figure 2, and chemical bond or mechanical interlocking bond between filler and HDPE could be the reason for higher thermal stability of C102 and C104 compared to C100 and pure HDPE.

By comparing the thermal degradation behavior of HDPE, C100, C102, and C104, it can be observed that all samples exhibit different degradation stages: HDPE showed three well-defined degradation steps at 357°C, 394°C,

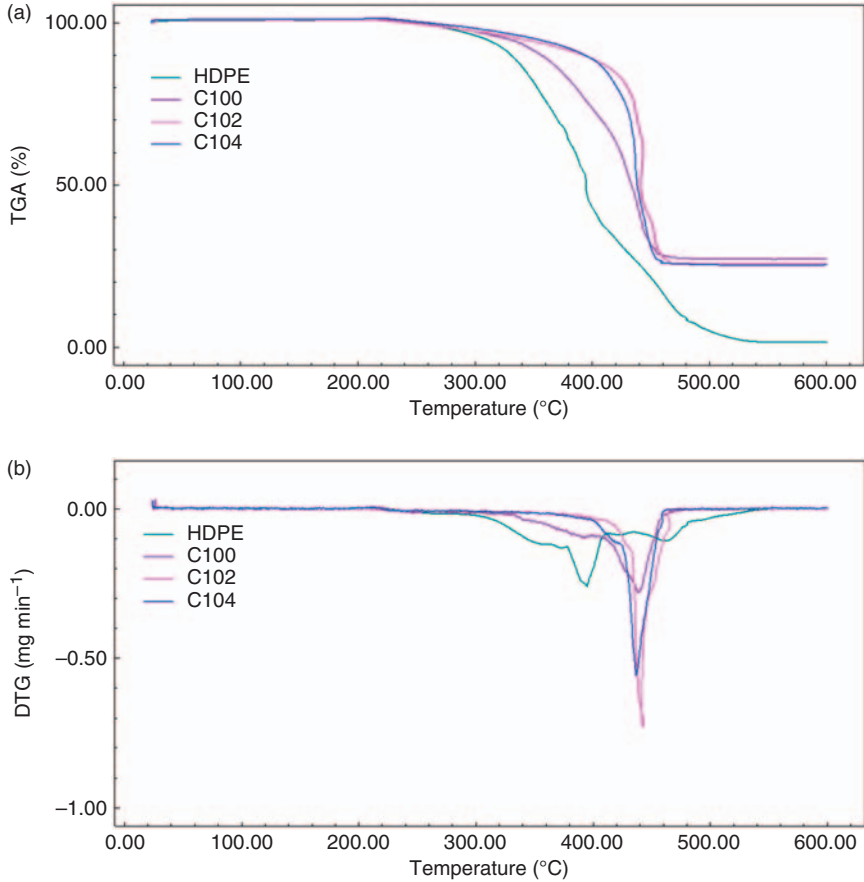


Figure 7. (a) TGA curves of HDPE and its nanocomposites at heating rate of 10°C/min and (b) DTG curves of HDPE and its nanocomposites at heating rate of 10°C/min.

and 462°C; on increasing the CaCO₃ content and surfactant HDPE exhibited only one weight loss.

CONCLUSIONS

To clarify the role of surfactant on thermal stability of HDPE nanocomposites, a series of HDPE/10 vol% CaCO₃ nanocomposites with different SA content were produced. Dimensional stability and thermal expansion coefficient were obtained using dilatometry test. In addition, the TGA tests were used to determine the thermal degradation of

HDPE/CaCO₃ nanocomposites. The results of the current study can be summarized as follows:

- Addition of nano-sized CaCO₃ to HDPE results in improvement of its dimensional stability.
- Thermal expansion coefficient of HDPE nanocomposites depends on SA content.
- Dimensional stability of HDPE filled by coated CaCO₃ are lower than that of pure HDPE and uncoated CaCO₃/HDPE composite.
- The thermal degradation of pure HDPE occurs at two stages. On increasing the nano-sized CaCO₃ particles and surfactant, degradation of HDPE occurs at one stage.

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