Influence of Alumina Particles on Thermal Behavior of High Density Polyethylene (HDPE)

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This study evaluated the effects of alumina (Al_2O_3) particles on thermal properties of High Density Polyethylene (HDPE). HDPE and HDPE/5, 10 & 15 wt% Al_2O_3 composites were prepared by compression molding. Differential scanning calorimetery (DSC) was used to analyze the thermal and crystallization behavior of the samples. The results indicated that the alumina particles affected the crystallization behavior of HDPE matrix, significantly. However, the DSC results showed that alumina content did not influence the melting temperature of HDPE in this composite. The results also showed that the incorporation of alumina particles caused the decrease of specific heat capacity coefficient and entropy.

Keywords Crystallinity behavior; HDPE/alumina composite; Thermal properties

INTRODUCTION

In recent years, the use of thermoplastic polymer matrix composites is increasing in automobile and industrial applications, but its vast application has been limited due to their low thermal and mechanical properties. Mineral fillers are often compounded into thermoplastic polymers to improve the properties of thermoplastics can be changed. Increase of the thermal conductivity[1,2], dimensional stability[3], thermal degradation[4,5] crystallinity[6–9], strength[4,6–7,10–12], etc. results when the secondary phase is added as filler to a thermoplastic polymer matrix. Tavman showed that the tensile strength, elongation at break and toughness decreased with increasing copper content, attributed to the introduction of discontinuities in the structure[1]. The modulus of elasticity and thermal conductivity increased with increasing copper content. Herzig and Baker showed that the relatively small additions of the Calcium carbonate filled polypropylene resulted in small increases in absorbed impact energy[13].

The addition of calcium carbonate to polyethylene increases impact strength in the investigated temperature range of −40 to +70°C and alters the primary micromechanism of plastic deformation from crazing–tearing and brittle behavior in neat polyethylene to particle-induced cavitation and fibrillation in the composite[14].

The mechanical and physical properties of composites using particulate fillers are influenced strongly by many parameters such as particles shape[15], particles size[15,16], the loading of fillers concentration[17], type of matrix, microstructure, and interfacial interaction between particles and matrix[18].

Polyethylene (PE) is one of the most widely used semi-crystalline polymers in industry. To improve the thermal and mechanical properties of HDPE, the addition of filler sand rigid particles is very common. Alumina particles as a mineral filler, causes change of the physical, thermal, and mechanical properties as well as in the crystallinity behavior of polymers. Murty et al. studied the influence of metallic additives on thermal degradation and melting of high density polyethylene (HDPE)[19]. They showed that the addition of alumina particles to HDPE caused an increase in the degradation temperature of polymer compared to other metallic additives such as $CaCO_3$, CuO and ZrO_2.

Because there is not any evidence of a paper focused on the role of alumina particles on thermal properties of HDPE composites, the main goal of this research was to find out the effects of alumina particulates such as filler on thermodynamic properties of high density polyethylene.

EXPERIMENTS

High density polyethylene (HDPE) was supplied by Tabriz petrochemical complex, Iran. A 99.99% pure alumina was obtained from Shimadzu Co., Japan. The alumina weight percent in composite sample was about 10. The distribution of alumina particulates was determined by using a particle–size analyzer device. Figure 1 shows
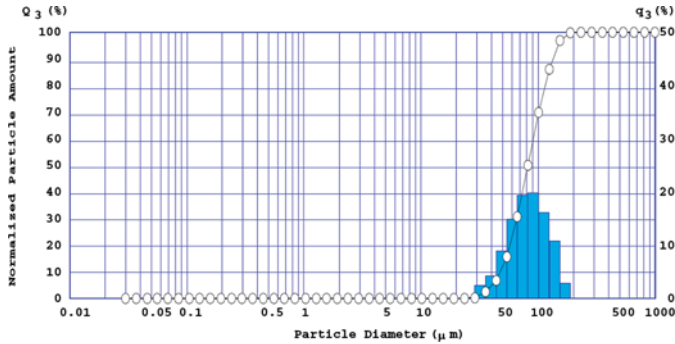
FIG. 1. The variation of normalized particle amount versus particle diameter. (Color figure available online.)
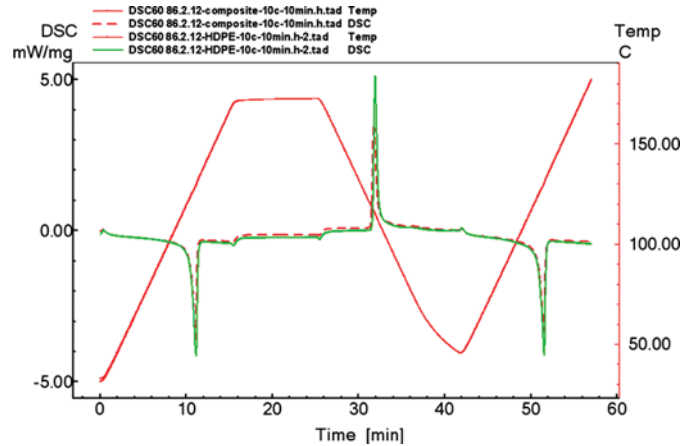

FIG. 2. The variation of power used for increasing temperature for HDPE and its composites versus time and temperature. (Color figure available online.)

the variation between the normalized particle amounts versus particle diameter. As it can be realized from this figure, the particicule's diameter are in the range of 23.538-232.7 μm and their mean diameter is about 80.472 μm.

Alumina particles and HDPE were first mechanically mixed to achieve HDPE/(5, 10 and 15) wt% of alumina composite. The premixed HDPE and alumina particles were squeezed between glass sheets, and heated at about 150°C under pressure for 5 min, followed by cooling to room temperature.

The thermal properties of pure HDPE and its composite were measured using heat flow differential scanning calorimetry device (Shimadzu DSC, model DSC 60). At first, the instrument was calibrated using the onset temperature of melting and fusion enthalpy of Indium standard. Samples were between 2–3 milligrams in weight.

The material was crimped in an aluminum pan using a simple press. For determining thermal properties, the samples were heated from room temperature to 200°C at a heating rate of 10°C/min, held there at 200°C for 10 min to eliminate remaining crystals, and immediately cooled at the same rate to room temperature. In the second heating cycle, the samples were heated under a similar condition to first heating cycle. At least two specimens for each type of materials were tested by DSC tests, and the average values were reported.

RESULTS AND DISCUSSION

Figure 2 illustrates the variation of power used to increase the temperature to run the DSC thermograms of HDPE and its composites, during the first heating, cooling and second heating cycles. In DSC curves, the first and the third peaks show melting phenomena and endothermic peaks, while the exothermic peak 2 belongs to solidification phenomena. According to Figure 2, the amount of power used decreased with the incorporation of alumina particles to HDPE matrix.

The main reason for this reduction is related to lower specific heat capacity of particles when compared to the pure HDPE and a smaller fraction of HDPE in the sample.

The heat of fusion and solidification, melting (TPf) and solidification (TPC) temperature, crystallinity index and initial (TCi, TCf) and final (Tfi, Tff) temperature of solidification and fusion peaks were obtained from DSC curves and summarized in Table 1.

As seen in Table 1 and Figure 3a, the melting temperature and fusion duration of composite were similar to the pure HDPE, but significant effects were shown in the solidification process. The initial solidification temperature of the composite was higher than the HDPE. Furthermore, the solidification duration increased a little according to Table 1 and Figure 3b.

The crystallization temperature increasing could be explained by the presence of alumina particles in polymer matrix, which could act as nucleation sites[20]. The DSC results also showed that the fusion and solidification heat amounts of HDPE/alumina composite are lower than pure HDPE. The main reason for reduction of heat transformation (fusion and/or solidification) was related to the decreasing of volumetric polymer fraction in composite and lower specific heat capacity of alumina particles.

The fusion heat, which was determined by the integration of heat flow curve, was used to calculate the crystallinity index of HDPE and its composite. Crystallinity ratio is defined by:

$$X = \frac{\Delta H_{fusion}}{\Delta H^\circ} \tag{1}$$

where X, ΔH_{fusion} and ΔH° are the crystallinity index, fusion enthalpy, and fusion heat for perfect crystalline HDPE, respectively. The value of fusion heat for perfect crystalline HDPE is taken as 70 cal/g by Wunderlich[21].

According to equation (1), the crystallinity indexes of HDPE and its composites were calculated and summarized

TABLE 1
The heats of fusion and solidification, melting (T_{Pf}) and solidification (T_{PC}) temperature, crystallinity index and initial (T_{Ci}, T_{Cf}) and final (T_{fi}, T_{ff}) temperature of fusion and solidification peaks

Cooling cycling				Second heating cycling			
T_{ci} (°C)	T_{cf} (°C)	T_{cp} (°C)	Enthalpy (j/g)	T_{fi} (°C)	T_{ff} (°C)	T_{fP} (°C)	Enthalpy (j/g)
HDPE	117.03	110.94	115.25	158.38	123.9	132.67	130.18	179.54
PE.5 vol%AL$_2$O$_3$	118.02	111.66	116.09	147.29	123.2	132.84	130.35	166.18
PE.10 vol%AL$_2$O$_3$	118.91	112.09	116.13	130.6	123.03	133.17	129.99	136.54
PE.15 vol%AL$_2$O$_3$	118.80	112.24	116.18	123.9	123.03	132.5	128.9	118.1

in Table 1. To investigate the behavior of polymer matrix in composite, the crystallinity index of this sample was divided into the weight percent of HDPE. Based on Table 1, the crystallinity index decreased when the weight percent of Alumina particles increased.

The crystallinity degree reduction of composites could be explained by the presence of alumina particles, which were situated in the amorphous structure of polymer matrix[22]. Consequently, the crystal domain of polymer

FIG. 3. (a) The thermographs of HDPE and its alumina powder composite which was crystallized; (b) DSC melting curves of HDPE and its composites. (Color figure available online.)

matrix was reduced. On the other hand, they caused an increase in the solidification time required for ordering the polymer chains.

The reduction of crystal domain and increasing of crystallization time have an indirect and a direct relationship with crystallinity degree. According to DSC results, the augmentation of the amorphous domain of HDPE in composite dominated the solidification duration.

The crystallinity index of semi-crystalline thermoplastic polymers could be determined by nucleation and growth rate of spherolite. By using DSC test, nucleation and growth rate of spherolites could be simply calculated.

The subtraction of crystallization temperature corresponding to the maximum of the crystallization peak, and the onset temperature corresponding to the beginning of the crystallization phenomena $T_p - T_{ci}$, are inversely proportional to spherolites growth rate[23]. The slope of the peak at the end of solidification has an indirect relationship with the germination rate or the nucleation rate[23].

As can be seen from Table 1, $T_p - T_{ci}$ or spherolite growth rate did not change by the addition of alumina particles in HDPE matrix. The nucleation rates as the invert slop of the peak at the end of solidification were 1.68, 0.86, 0.8 and 0.7 for pure HDPE, HDPE/5, HDPE/10 & HDPE/15 wt% AL$_2$O$_3$ composites, respectively. The insensibility of growth rate and the rising nucleation rate of of spherolite were other reasons for the decrease in the crystallinity index in composite.

According to Figure 3b, the relative crystallinity fraction was calculated by the following equation (2)[18]:

$$X(t) = \frac{\int_0^t \left(\frac{dH}{dt}\right) \times dt}{\int_0^\infty \left(\frac{dH}{dt}\right) \times dt} \qquad (2)$$

The first integral is the heat generated at time t and the second one is the total heat when the crystallization is completed.

Relative crystallinity versus temperature for HDPE and its composite are shown in Figure 4. As seen from this figure, solidification in composite occurred in a wide
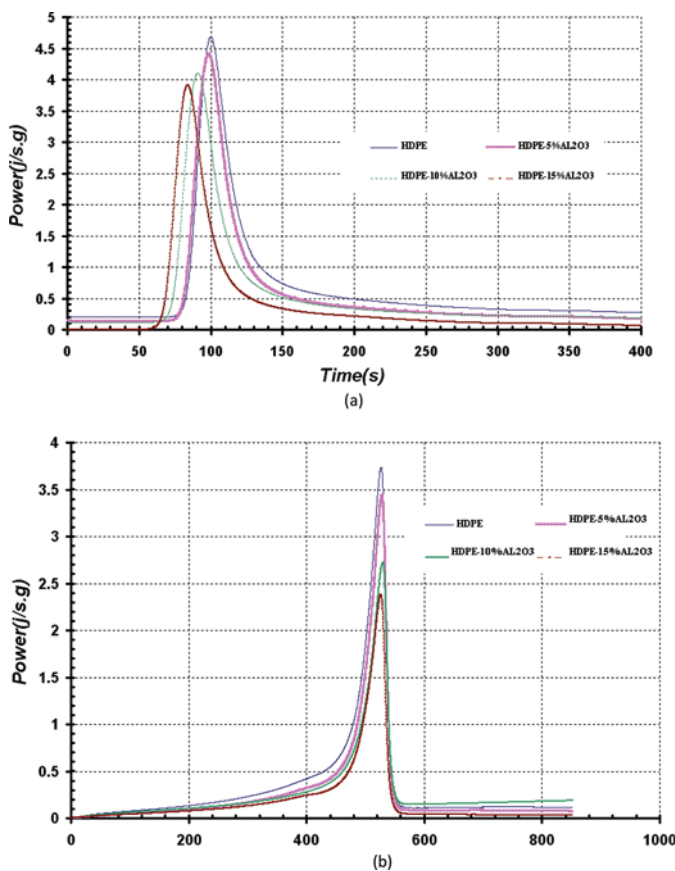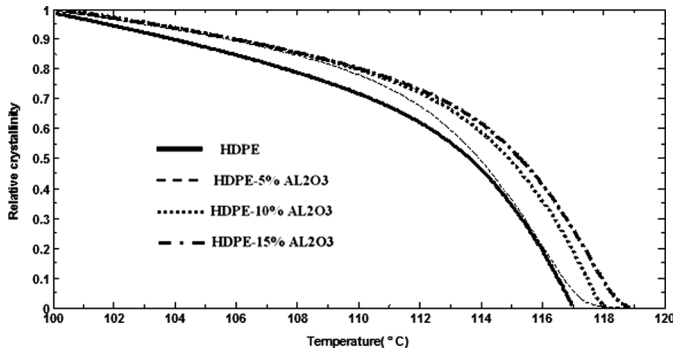
FIG. 4. Relative crystallinity versus temperature during crystallization of HDPE and its composites.

FIG. 6. Plots of the variation of $\ln[-\ln(1 - X_t)]$ versus ln (t) for HDPE and its composites.

temperature range, and crystallization started at a temperature higher than the neat polymer.

Figure 5 shows the relative crystallinity varying time for HDPE and it's composites. As could be realized from this figure, the increase of the solidification time and the change in solidification rate were obtained by the addition of alumina as a filler in HDPE matrix.

Relative crystallinity changes over time could be readily evaluated by the following:

$$X(t) = 1 - \exp(-kt^n) \qquad (3)$$

where x(t) is a relative crystallinity at time t, n is the Avrami index that provides a qualitative indication of the nucleation mechanism and on the form of crystal growth, and k is the constant including nucleation and growth parameter, the constant k increases with the decrease of crystallization temperature[24].

Equation (3) could be transformed into logarithmic form:

$$\ln[-\ln(1 - X_t)] = \ln(k) + n\ln(t) \qquad (4)$$

Applying Avrami theory, when $\ln[-\ln(1 - X_t)]$ is plotted against $\ln(t)$, a straight line is obtained with the slop as n and the intercept as ln (k). The plot of $\ln[-\ln(1 - X_t)]$ versus
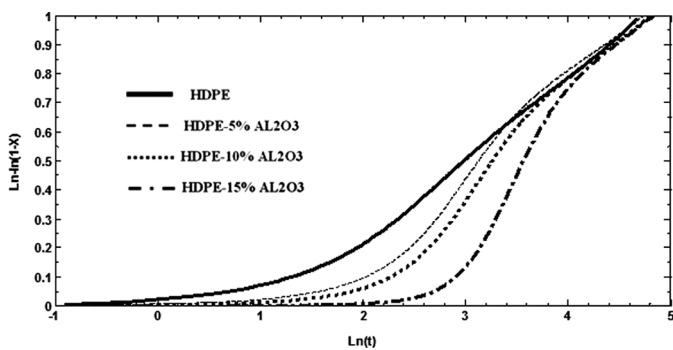
time is shown in Figure 6. Based on this figure, the Avrami kinetic parameters (i.e., k and n) could be obtained and summarized in Table 2 for HDPE and its composites.

According to values reported in Table 2, k constant decreased with increasing weight percent of alumina particles. Also, the Avrami exponent increased when the weight percent of alumina particles increased. Avrami index 3 suggests an instantaneous nucleation with spherolite growth geometry. It seems that the nucleation mechanism and spherolite growth rate of HDPE were changed when alumina particles were doped to the matrix, and the similar nucleation mechanism and spherolite growth rate were shown in HDPE/15%wt Al_2O_3 composite.

The Avrami plots exhibited a deviation from linearity at the later stages of crystallization at some crystallization temperatures. This deviation has been attributed to the occurrence of second crystallization[25,26].

The reduction of k values revealed that these particulates had significant effects on the crystallization temperature, spherolites nucleation, and growth rate.

The variations of power used versus temperature in heat cycling are shown in Figure 7. As expected, by addition of alumina to polymer matrix, the power used for rising temperature decreased for both solid and liquid phases. This effect was related to the lower specific heat capacity of alumina and polymer crystal domains in composite compared to the neat HDPE.

FIG. 5. The variation of relative crystallinity versus time of HDPE and its composites during none isothermal crystallization.
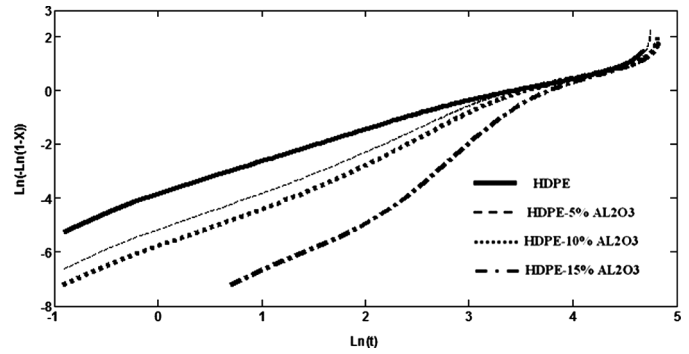
TABLE 2
Values of k and n at various cooling raters for HDPE and its composites

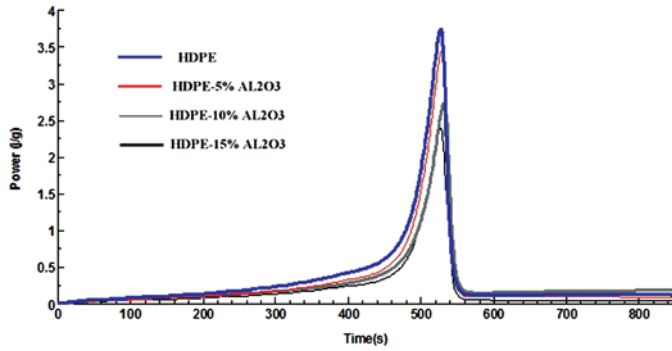| Samples	ln(k)	N
HDPE	−6.15	1.956
PE.5 vol%AL$_2$O$_3$	−6.965	2.1725
PE.10 vol%AL$_2$O$_3$	−7.0167	2.154
PE.15 vol%AL$_2$O$_3$	−10.956	2.972

FIG. 7. The variation of power used versus temperature for HDPE and its composites. (Color figure available online.)

FIG. 9. The variation of specific heat capacity versus temperature for HDPE 5, 10, 15 wt% Al_2O_3 composites. (Color figure available online.)

Sensible heat was obtained by the integration of power used versus time by using the following equation:

$$\Delta H_{T_1}^{T_2} = \int_{T_1}^{T_2} Q \cdot dt \tag{5}$$

where $\Delta H_{T_1}^{T_2}$, Q and t are sensible heat, the power used, and time, respectively. Figure 8 shows the curves of the sensible heat against temperature for HDPE, HDPE/5, HDPE/10 and HDPE/15 wt% Al_2O_3 composite. As could be observed, the values of sensible heat at both liquid and solid phases are lower than pure HDPE.

The reduction of sensible heat values could be mainly accounted for by the decrease of the volume percent of HDPE by the increase of alumina particles. Crystallinity indexes of HDPE also affected sensible heat. Generally, the crystal domain has a stronger Van der Waals force than the amorphous area. According to the drop in crystallinity index by addition of alumina particles to polymer, the amount of heat to rising temperature decreased. According to Figure 8 and by using the following equation, specific heat capacity was calculated:

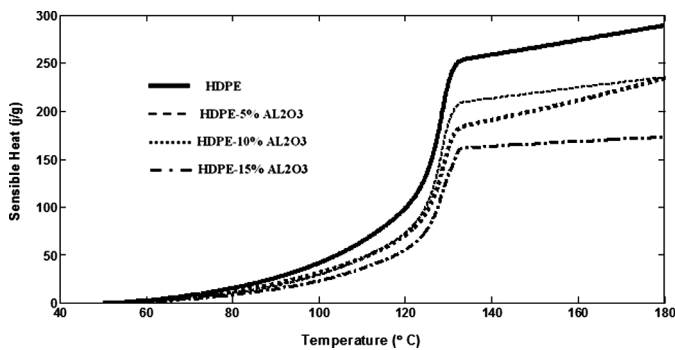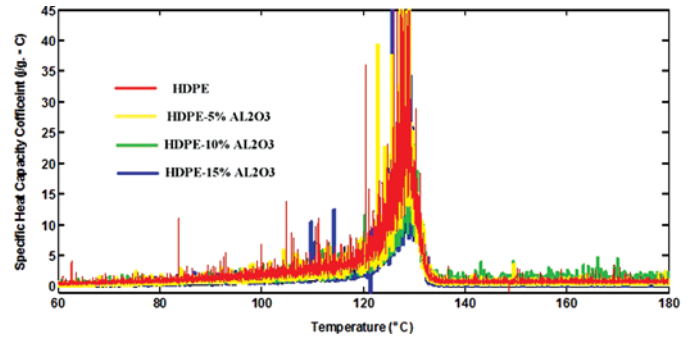$$\Delta Cp = \frac{\partial \Delta H}{\partial T} \tag{6}$$

where ΔCp, ΔH and T are specific heat capacity, sensible heat and temperature, respectively. In Figure 9, the variation of sensible heat of HDPE and its composites versus temperature are shown. As seen from this figure, the specific heat capacity of polymer for both liquid and solid phase was much more than its composites. The main reason for this reduction could be attributed to the lower volume of polymer and crystallinity index of polymer in composite in comparison with pure HDPE.

To compare the disordering of HDPE and HDPE in composite chains, the entropy was calculated by using the following equation:

$$\Delta S_{T_1}^{T_2} = \int_{T_1}^{T_2} \frac{\Delta Cp}{T} dT \tag{7}$$

where ΔCp, ΔS, and T are specific heat capacity, entropy, and temperature, respectively. The entropy variation of HDPE and its composites versus temperature are shown in Figure 10.

Generally, for all materials, by increasing temperature, the amount of entropy increases. By rising the temperature, the variation of entropy for HDPE was much more than composites at both liquid and solid phases. This could refer

FIG. 8. Curves of the sensible heat against temperature for HDPE and HDPE/5, 10, 15 wt% Al_2O_3 composites.
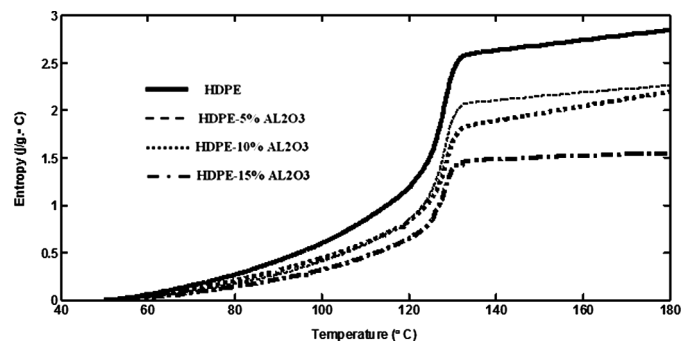

FIG. 10. The variation of entropy versus temperature for HDPE and its composites.

to the reduction of the of polymer volumetric fraction in the composite. Additionally, alumina particles restricted the motion of HDPE chains. Of course, lower crystallinity index had an indirect relationship with entropy variation. But the summation of lower polymer volume, the mobility of chains, and the crystallinity index of composite cause a decrease in entropy variation with respect to pure HDPE.

CONCLUSION

In the current study, in order to investigate the thermal properties of HDPE and its composites, DSC were used. The results of the current study are summarized:

1. The melting temperature of HDPE and its composites were the same value, but crystallization temperature increased by the addition of alumina particles in HDPE matrix, indicating that the particles act as nucleation sites.
2. The crystallinity index decreased by the addition of a mineral filler to HDPE matrix.
3. The presence of alumina particulates caused a decrease in the Avrami index and a change in the nucleation and growth rate of spherolite.
4. Sensible heat, transformation heat, specific heat capacity and entropy of polymer matrix decreased when the weight percent of alumina particles increased.

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