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Influence of nanoparticle weight fraction on morphology and thermal properties of HDPE/SiO_2 composite films

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High-density polyethylene (HDPE) composite films with different amounts of SiO_2 nanoparticles ($1-20$ % vol.) were prepared by melt blending using a high-pressure thermal pressing technique. The morphological characterization, surface topology and distribution of nanoparticles in polymer matrix of nanocomposites were investigated by using Scanning electron microscopy (SEM) and atomic force microscopy (AFM). The thermal characterization of the nanocomposites were investigated by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). SEM and AFM results revealed that silica nanoparticles aggregates were distributed mainly homogeneously. The nano-fillers change supramolecular structure and surface morphology of HDPE strongly. DSC results showed addition of nano-SiO_2 particles slightly decrease the melting temperature by 3-4 degree but strongly decrease the crystallization temperature by 7-8 degree. And crystallinity degree of the HDPE decrease. The thermal stability of the composite films was measured using Thermo Gravimetric analysis (TGA). Polymer nanocomposite showed higher thermal stability as compared with pure HDPE. Composites with 20 % vol. of nano-SiO_2 have maximum thermal degradation temperature of 498.4 ° C.

Keywords: high-density polyethylene, nanocomposite films, SiO_2 nanoparticles, degree of crystallinity, thermal stability.

Introduction

In recent years, inorganic nanoparticles filled polymer composites have received increasing research interests of materials scientists because the filler/matrix interface in these composites might constitute a much greater area and hence influence the composites properties to a much greater extent at rather low filler concentration as compared to with traditional composites [1].

Polymer nanocomposite materials are manufactured commercially for many diverse applications such as isolation materials, aerospace components, automobiles, etc. In the field of nanotechnology, polymer based nanocomposites have become an important area of current research and development. The addition of inorganic spherical nanoparticles to polymers allows the modification of the polymers physical properties as well as the implementation of new features in the polymer matrix. The structure of nanocomposites is essentially established by the arrangement of the particles in the polymer matrix. The particles may be dispersed as individual primary particles or as aggregated particles (secondary particles) [2].

The development of polymer nanocomposites has been an area of high scientific and industrial interest in the recent years, due to several improvements achieved in these materials, as a result of the combination of a polymeric matrix and, usually, an inorganic nanomaterial. The improved performance of those materials can include mechanical strength, toughness and stiffness, electrical and thermal conductivity, superior flame retardancy and higher barrier to moisture and gases. Nanocomposites can also show unique design possibilities, which offer excellent advantages in creating functional materials with desired properties for specific applications. The possibility of using natural resources and the fact of being environmentally friendly have also offered new opportunities for applications [3].

The dispersion of nanometer-sized particles in the polymer matrix has a significant impact on the properties of nanocomposites. The great differences in the properties of polymer and silica materials can often cause phase separation. Therefore, the interfacial interaction between two phases of nanocomposites is the most decisive factor affecting the properties of the resulting materials [4].

Silica/polymer composites have attracted an interest in various application fields: metal uptake, sensors, electronics and optical packaging materials, photoresist materials, optical devices, flame-retardant materials, proton exchange membranes, anticorrosion materials grouting materials, oil adsorbents, biomedical materials, other coatings, etc. They also exhibit unique properties such as optical transparency, specific electrical, weathering and abrasion resistance [5].

The silica has an extremely large surface area and smooth nonporous surface, which could promote strong physical contact between the filler and the polymer matrix [1]. SiO_2 nanoparticles have high surface area and enhanced reactivity of the surface. For instance, they are broadly used in catalysts, chemical sensors, chromatography and ceramics [6]. Nanoparticle addition into polymer matrix produces nanocomposites with improved mechanical strength, resistance to wear, and thermal stability [7].

Silica nanomaterials of various morphologies (meso/micro porous spheres, hollow spheres, ribbons, tubes, rods, cubes and so on) are attracting an increasing attention due to their potential application in catalyst supports, drug carrying and release, chiral separation, sensors, cell imaging, liquid crystals, antireflection coatings etc. Mesoporous silica could be used to store and release drugs and chemicals, and so on [8].

The interphase thickness in the grafted nanoparticle composites increases with the percentage filler. A thicker interphase is not bound to improve nanocomposite performance. If the miscibility between the components is good enough, a thicker interphase would be beneficial to the interfacial adhesion and hence the mechanical properties [9].

Recently, a large number of silica/polymer composite materials have developed for various application due to their unique properties combining the advantages of the inorganic fillers and the organic polymers. There are drawbacks in the development of these composites such as the incompatibility of silica with organic polymer and nano sized hybridization. And for overcome this problem, understanding the interfacial interaction is critical issues. In spite of the fact that a lots of researches on the development of polymer/silica nanocomposites has already been reported, more detailed study of the polymer matrix-filler composite structure is required [10].

The aim of the present work is to investigate the effect of the nano-SiO_2 particles filler over morphological structura and thermal stability of high-density polyethylene.

Materials and methods

Nanocomposite films consisting of high-density polyethylene matrix (HDPE) filled with amorphous silica dioxide α-SiO_2 of spherical morphology were prepared by thermal pressing (under a pressure of 15 MPa) at a temperature $165\,^{\circ}C$, followed by rapid cooling in water-ice system. The reference HDPE foils for comparative experiments were prepared in the same manner but without the nanoparticles. The composite samples were made as thin films; the thickness and the diameter were 80-100 μm and 5 cm, respectively. The volume fraction of the nano filler in the polymer matrix was 1, 3, 5, 10, and 20 % vol. While producing film samples it was used the following reference [11].

Melt blending is the most commonly used method in composite preparation due to its efficiency and operability. In the process, The inorganic filler (i.e., silica) are mixed with the polymer in its melt at a temperature equal or greater than the melting point of the polymer.

Under the suitable conditions composite with the necessary properties can obtained. This technology is very versatile and can be applied to obtain varius polymers [12].

The most conventional and simple method to prepare polymer nanocomposites is direct mixing of polymer and nanofillers by melt and solution mixing. Melt mixing is usually associated with a high temperature melting process, nanoparticles are filled into melting polymer and dispersed by shear forces, and then the nanocomposites are obtained by pressing or extrusion molding process. This method is mainly suitable for thermoplastic polymers, which can be pliable and moldable above softening and melting temperatures. The drawback of such a mixing process is that the mobility of polymer chains is still limited even at the molten state [13].

As a filler it has been used an amorphous silica dioxide α-SiO_2 (Sky Spring Nanomaterials, Inc. Houston, USA) with size of 20-30 nm spherical particles, specific surface area of S=160 m^2/g and density of 2.65 g/cm^3 [14].

Powdered high-density polyethylene (grade 20806-024) with an average molecular weight of $95 \cdot 10^3$ g/mol, crystallinity degree of ca. 60 %, melting point of 130 ° C, and density of 958 kg/m^3 was chosen as a polymer matrix.

Atomic force microscopy (AFM). The morphological features of HDPE+%SiO_2 polymer nanocomposite films were analyzed by NTEGRA PRIMA microscope at semi contact mode with commercial NSG01_Au tips of 10 nm curvature radius (NT-MDT Spectrum Instruments, Zelenograd, Russia) at room temperature. Scan size was 10×10 microns. The scanning rate and scanning lines number on the image are 0.3-0.5 Hz correspondingly.

Scanning electron microscopy (SEM). The surface fracture of composite films morphology and distribution of SiO_2 nanoparticles in the polymer matrix has been studied by scanning electron microscopy using cryogenically fractured samples. By immersing the samples in liquid nitrogen, a brittle fracture is obtained avoiding large deformations on the examined surface. Morphological studies were performed using JEOL JSM-6490LV SEM instrument, operating at an accelerating voltage of 10-20 kV.

The melting and crystallization characteristics were obtained using a differential scanning calorimeter (DSC) NETZSCH 204 F1 Phoenix. Temperature and sensitivity calibration was performed at the same conditions as sample measurement. Calibration measurements were done in Ar atmosphere. Samples of approximately 10 mg were placed in a closed aluminum pan (Al 99.5 Max, 600 ° C crucibles with 6 mm diameter and 25/40 μl volume) and were heating at a rate of 10 ° C/min. An empty pan was used as a reference in the measurements. The DSC instrument was programmed to execute the analysis in two cycles. In the first cycle the samples were heated from 25 to 180 ° C. In the second cycle the crystallization curve was obtained by cooling the samples to 25 ° C. All samples were scanned in argon atmosphere (40 mL/min) at a heating rate of 10 ° C/min. The melting temperature and crystallization temperature were obtained from maxima of the endothermic and exothermic peaks, respectively.

The thermal degradation and the mass loss studies of the samples were carried out in TGA 209 F1 Libra (Netzsch) gravimeter. Approximately 10 mg of the samples were degraded under argon flow (20 mL/min) in the thermo balance under dynamic condition at the heating rate of 10 ° C/min. The composite samples were scanned in the temperature range of 30-1000 ° C. The filler content left at 1000 ° C, the thermal characteristics (onset degradation temperature (T_{on}), temperature at maximum rate of degradation (T_{max}), temperatures at different mass losses) were calculated from the TG curves. Samples were placed in an Al_2O_3 pan (99.7 Max. 1700 ° C crucibles with 6.8 mm diameter and 85 μL volume).

Results and discussion

Morphological characteristics AFM

In Figure 1 are presented the surface morphological 2D images (left) of HDPE+(1-20 vol.%)SiO_2 nanocomposites and the histogram of size distribution of aggregates of SiO_2 nanoparticles (right). The upper row presents the 2D topography images of 10×10 μm^2 area. Surface morphological imaging of the composite films by AFM revealed uniform distribution of the SiO_2 nanoparticles aggregates on the surface of the polymer matrix. The SiO_2 nanoparticles show very well dispersion in high-density polyethylene matrix. There is not strong aggregation of SiO_2 nanoparticles. The aggregates formed mainly at higher filler concentrations. Agglomeration of nano SiO_2 can also be explained in terms of van der Waals forces between the nanoparticles. With the increase in amount of nanoparticles, there is a significant decrease in the particle-to-particle distance therefore the effect of attractive forces between the nanoparticles becomes more significant. It subsequently leads to more formation agglomeration of nanoparticles. Size distributions of aggregates have Gauss form (Figure 1).

With the increase in volume content of nano-fillers in polymer, there is an increase in aggregate size. At the volume content of SiO_2 in polymeric matrix 1% the sizes of forming aggregates vary in interval 40-60 nm and at 5% the average sizes vary 70-100 nm (Table 1). Overall AFM studies demonstrated that with addition the nanoparticles to the polymer matrix a change in supramolecular structure and surface morphology of HDPE.

Table 1.
Characterization of aggregates of the HDPE/SiO_2 polymer nanocomposite films evaluated by AFM analysis.

Filler content ω, vol. %	Surface area, nm^2	Average size, nm	Length, nm	Volume, nm^3	Diameter, nm
1	3620	56.6	90	19700	63.8
5	12090	42	68.9	9810	67.4
10	15880	70.9	116	37600	81.3
20	21400	42.9	69.5	8890	98.4

Surface Morphology and Nanoparticles Dispersion

The morphological and structural analysis of nanocomposite films was provided by scanning electron microscopy (SEM). The SEM micrographs of the fracture surfaces of HDPE/SiO_2 composite films with various percentages of SiO_2 nanoparticles were studied. Each sample has six images with different magnifications (Figure 2 and Figure 3). SEM micrographs for all nanocomposite films revealed that the SiO_2 nanoparticles are uniformly dispersed in the polymer matrix. With the addition of nano-SiO_2, the fracture morphology is changed and the fracture surface becomes obviously uneven as shown the fracture morphology of the composite films with nano-SiO_2. Different morphology for composite films with 5 and 10 vol. % SiO_2 filler concentration was observed.

The morphological studies by the SEM method of HDPE/SiO_2 composites showed that the introduction of an inorganic filler leads to the formation of

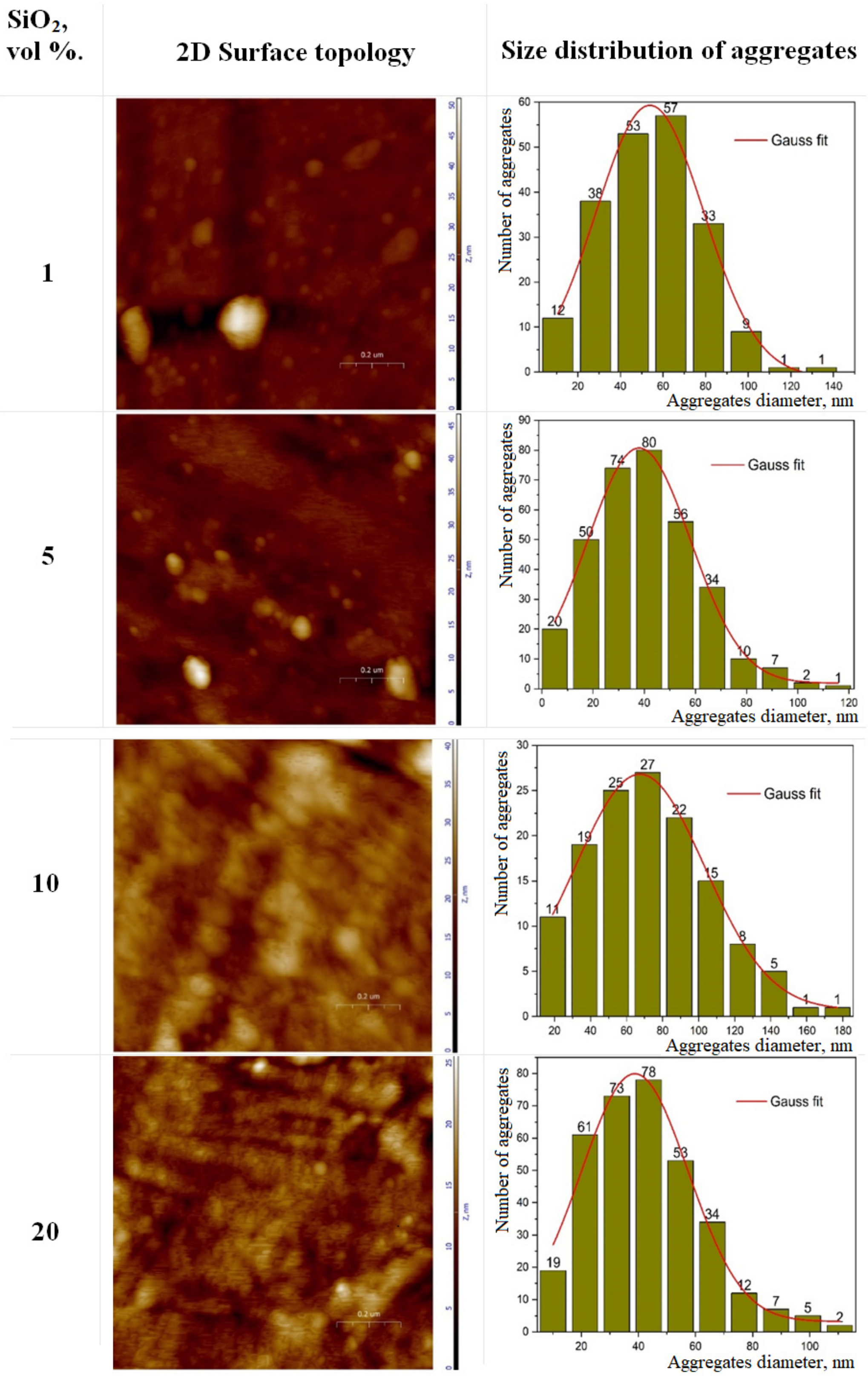

Figure 1. The surface topology images of HDPE/SiO $_2$ nanocomposites and size distribution of aggregates of SiO $_2$ nanoparticles.

aggregation structures. An increase in the content of the filler leads to an increase in the dimensions of aggregates. It should be noted that there are no inclusions of filler particles in the bulk of the polymer matrix in the composites. The structural

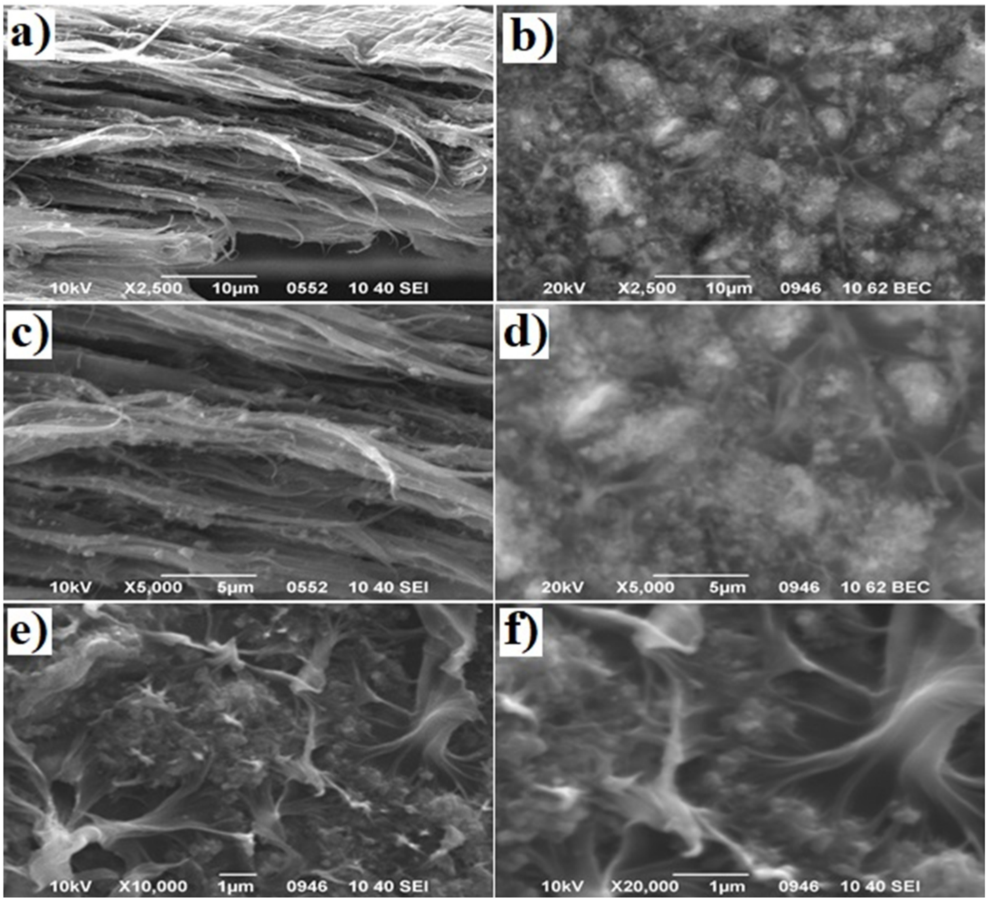

Figure 2. The fracture surface morphologies of HDPE+5%SiO$_2$ polymer nanocomposite films: (a) and (c) - × 2500; (b) and (d) - × 5000; (e) × 10000; (f) × 20000.

changes appeared in increased in the degree of crystallinity, which affects the morphology of polyethylene in the form of reduced elasticity. It should be noted that morphological changes were not observed only in the volume of the composite, but also on the surface of the film material.

The analysis exhibited that addition of 5 % SiO$_2$ leads to a change in the morphology of the polymer. And, fillers as the form of compact particles filled in the cavities of a polyethylene matrix with a size of 1-2 μm. Also, an increase in the filler content up to 20 % leads to an increase in cavity sizes up to 5 μm. On the whole SiO$_2$ nano-paticles are strongly bind with polymer.

Increased content of SiO$_2$ leads to a larger agglomerates because of the formation of hydrogen bonds among the abundanthydroxyl groups and adsorbed water on their surface and hence greater probability of debonding due to the poor inter facial adhesion.

The observation of the fracture surfaces of the composite films revealed that the increasing filler content leads to pronounced fibrils structure deformation of HDPE. The fact that nanoconfined regions formed around the nanofillers aggregations cause density fluctuations and disturbed chain mobility leading to different extents of deformations of the polymer fibrils was confirmed through the fractography images. The fact that the large filler aggregations constitute the stress concentrations which lead to fracture was also confirmed through the obtained images.

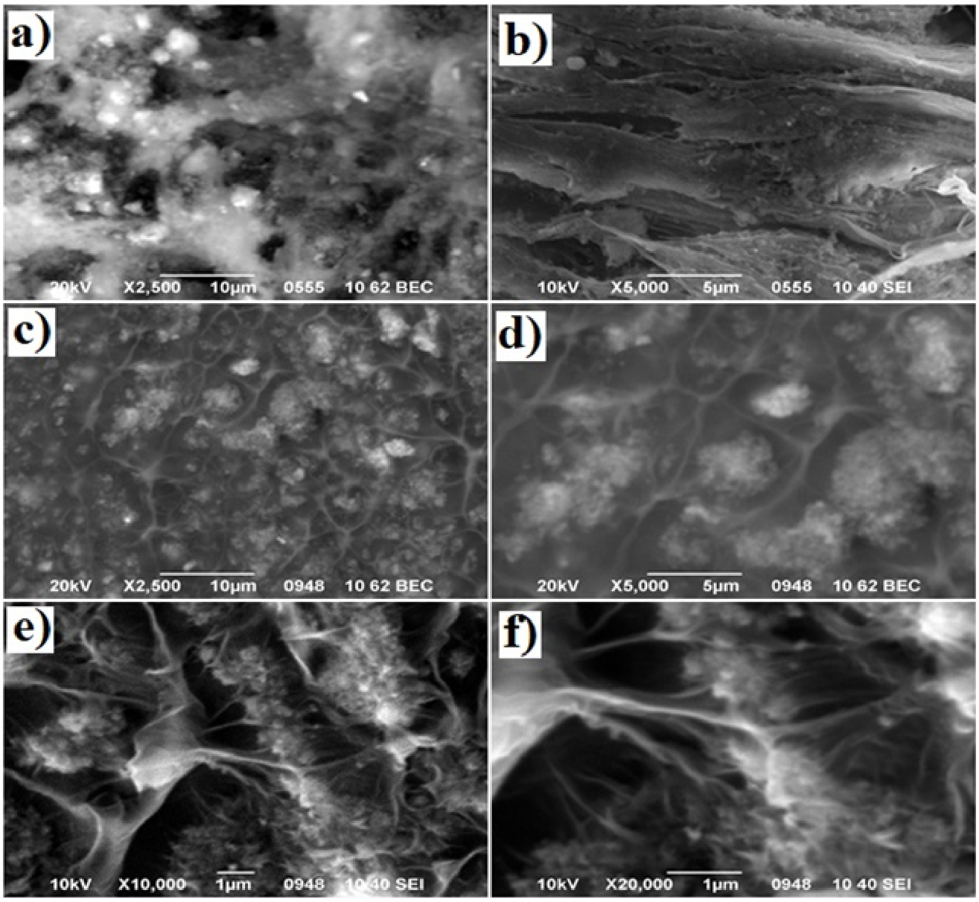

Figure 3. The fracture surface morphologies of HDPE+10%SiO_2 polymer nanocomposite films: (a) and (c) - × 2500; (b) and (d) - × 5000; (e) × 10000; (f) × 20000.

Differential scanning calorimetry (DSC)

DSC analysis was performed to study the effect of SiO_2 nanoparticles on the thermal behavior and crystalline structure of HDPE/SiO_2 composite films. Figure 4 (a, b) are demonstrated the DSC heating and cooling thermograms for the virgin HDPE and the HDPE+%SiO_2 nanocomposites. The melting temperature (T_m) and the enthalpy of fusion (ΔH_m) for the nanocomposites were obtained from the heating curve. The crystallization temperature (T_c) was obtained from the crystallization curve. The degree of crystallinity of the virgin HDPE and its polymer nanocomposites (X_c) was calculated by

$$X_c = \frac{\Delta H_m}{(1-\varphi)\Delta H_m^0} \times 100\%, \tag{1}$$

where, ΔH_m is enthalpy of fusion of the sample, ΔH_m^0 is heat of fusion for 100% crystalline HDPE, and φ is the weight fraction of the filler (SiO_2) in nanocomposites. Relative crystallinity was calculated assuming the heat of fusion of 100% crystalline polyethylene ΔH_m^0 to be 293 J/g [15]. The lamellar crystal thickness l_c was calculated using the empirical Gibbs-Thomson equation as follows [15]:

$$l_c = \frac{2\sigma_e \times 10^3}{\Delta H_m \rho_c (1 - \frac{T_m}{T_m^0})}, nm, \tag{2}$$

where, T_m and T_m^0 are experimental and theoretical melting point of polyethylene, respectively, and ΔH_m is the melting heat of unit volume, and σ_e is the lamellar surface free energy. The constant parameters for polyethylene are $T_m^0 = 145.7\,^\circ\mathrm{C}$, $\Delta H_m = 293\ \mathrm{J \cdot g^{-1}}$, $\sigma_e = 90 \times 10^{-3}\ \mathrm{J \cdot m^{-2}}$, and $\rho_c = 0.94\ \mathrm{kg \cdot cm^{-3}}$.

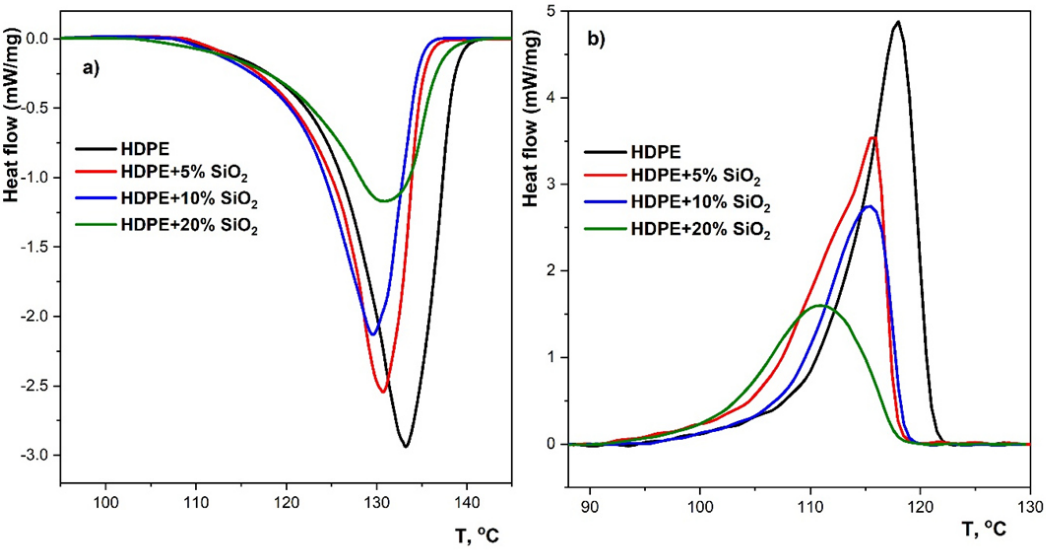

Figure 4. DSC thermograms for the pure HDPE and the HDPE+%SiO$_2$ nanocomposites: (a) 2nd heating and (b) 1st cooling cycles.

The DSC characteristic parameters of virgin HDPE and its nanocomposite films are listed in Table 2. For the virgin HDPE a melting temperature (T_m) is 133.2 °C and a crystallization temperature (T_c) is 117.9 °C. With increasing the content of SiO$_2$ in the composite the melting temperature slightly decreases by 3-4 degree as compared to the pure polymer matrix (Figure 4a and Table 2). And crystallization temperature decreases by 7-8 degree. Also, the degree of crystallinity of nanocomposite slightly decreases for the filler content from 0 % to 5 %, then slightly increases and stabilizes for the filler content from 5 % to 20 %. The detailed crystallization and melting characterization are summarized in the Table 2.

The crystallization time of the composite films was determined by

$$t = (T_0 - T)/\vartheta, \tag{3}$$

where T_0 is the initial crystallization temperature, T is final crystallization temperature, and ϑ is cooling rate.

Crystal size also referred to as crystal thickness or lamellar thickness in polymers, has also been estimated using DSC. Lamellar thickness (l_c) of HDPE increases with the addition of silica particles, which implies that silica aids the formation of more perfect crystals [16]. This can be attributed to the fact that silica particles act as heterogeneous nucleating agent inducing HDPE to form perfect and stable crystals. When the concentration of the nano-fillers increased beyond the optimum, the mechanical properties decreased significantly [17].

Table 2.
The DSC melting and crystallization characteristics for pure HDPE and its nanocomposites. Here: ω - filler content, T_m - melting temperature, T_c - crystallization temperature, ΔH_m – enthalpy of melting, l_c - lamellar crystal thickness and X_c - degree of crystallinity.

ω, vol. %	ω, mass. %	T_m, °C	T_c, °C	t, min	ΔH_m, J·g^{-1}	l_c, nm	X_c, %
0	0.0	133.2	117.9	0.89	-174.7	7.20	59.6
1	2.7	131.3	116.5	0.97	-159.1	9.28	55.8
3	4.6	130.8	115.7	1.07	-133.8	8.34	47.86
5	12.7	129.6	115.1	1.21	-126.2	8.03	49.34
10	23.5	129.3	114.3	1.45	-117.5	8.30	52.42
20	40.8	130.6	110.8	1.62	-90.22	8.23	52.01

This can be explained by the adhesive interaction between the polymer and nanofiller within the amorphous phase. Interfacial adhesion and filler dispersion are two of the most influential factors on the mechanical behavior of composite systems along with molecular and lamellar structure [18].

The SiO_2 nanoparticles are strong structural, thermodynamic and kinetic activity. Therefore, the presence of an active additive in HDPE leads to the fact that the polymer crystallization begins at a higher temperature, when the macromolecules have a higher mobility. This process is accompanied by the formation of larger crystallites and an increase in the degree of crystallinity of the polymer. During cooling of the HDPE, SiO_2 nanoparticles contribute to the transfer of its crystalline part to a more equilibrium state, and the amorphous (disordered) one to a less equilibrium state. The kinetic activity of SiO_2 nanoparticles is manifested in limiting the mobility of macromolecules and their stabilization in disordered (amorphous) regions of the crystallizing polymer [19].

Thermogravimetric analysis (TGA)

The thermal stability and mass loss of HDPE+%SiO_2 nanocomposite films were investigated by thermogravimetric (TGA) and differential thermal gravimetric (DTG) analysis. The mass loss curves of the composite thin films with 1-20 vol % SiO_2 nano filler are presented in Figure 5. An obvious enhancement of the thermal stability can be seen for all composite films. Indeed, a progressive increase in the thermal stability was found for increasing SiO_2 content. The mass losses of the composite films are in good agreement with their expected compositions (the highest difference is less than 2.5 %). How it's expected, at increasing filler content, the mass residue of nano-SiO_2 corresponds to mass loss. This confirms the successful fabrication of the nanocomposite films. It can be seen that the introduction of the filler increases the decomposition temperature of the polymer matrix composite, i.e., both T_{onset} and T_{end} values incrase with increasing filler loading.

The fact that these enhancements are observed in the early degradation stages (corresponding to small mass losses) but are not maintained as degradation proceeds is a very common phenomenon in materials degradation. The observed thermal stability enhancement can be attributed to the formation of more nanoconfined regions around the fillers and their aggregations as previously discussed, in which the local density fluctuations and hindered macromolecular chain mobility and dynamics lead to a chemical reactivity decrease and thus increase the thermal stability.

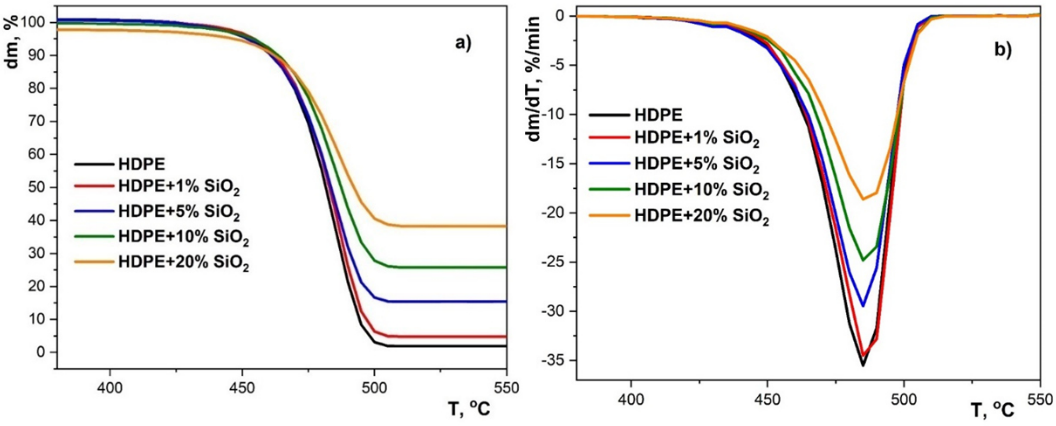

Figure 5. TGA curves (a) and its first derivative curves versus temperature (DTG) (b) of HDPE+%SiO $_2$ nanocomposite films.

Therefore, it is reasonable that an increased filler concentration would lead to a thermal stability increase. The mass residue observed in the mass loss curves also follows the expected increasing trend as the nanofillers are left as solid residues while polymer decomposes completely. The maximum rate of mass loss T_{peak} value slightly increases with the increase in filler loading (Table 3). Resulting data in terms of maximum weight loss (dm), extrapolated onset (T_{onset}) and endset (T_{end}) temperatures and the temperature for the maximum rate of mass loss (T_{peak}) are listed in Table 3.

Table 3.
The TGA and DTG results for HDPE and HDPE+%SiO $_2$ nanocomposite thin films. The ω - filler content, dm – mass loss, T_{onset} – onset temperature of degradation of polyethylene, T_{end} – final temperature of degradation of polyethylene, T_{peak} – the maximum rate of mass loss DTG temperature.

ω, vol. %	ω, mass.%	dm, %	T_{onset}, °C	T_{end}, °C	T_{peak}, °C
0	0.0	-100	462.8	495.5	485.5
1	2.7	-96.5	467.5	496.5	486.9
3	4.6	-91.8	467.8	495.6	485.3
5	12.7	-86.6	465.3	496.3	486.8
10	23.5	-75.8	467.4	497.8	486.9
20	40.8	-58.6	467.1	498.4	486.5

Conclusion

The AFM and SEM results points out that the SiO $_2$ nanoparticles are well dispersed in the HDPE matrix and thus confirming the successful fabrication of the nanocomposite films. Increasing the nano-SiO $_2$ filler content led to increase in formation aggregates and more brittle performance of the composites. For HDPE+%SiO_2 nanocomposite films observed slightly decrease in the melting temperature up to 4 ° C and decrease in the degree of crystallinity. This effect can be explained by the enhancement of polymer chain scission by the presence of the nanoparticles. The incorporation of SiO_2 particles shows strongly influence on the crystallization behaviour of polymer chains. The crystallization temperature of matrix in all composites is decreased about 8 ° C. From the thermal behavior of the composite films, the presence of nano-SiO_2 filler was found to lead to a great enhancement of the thermal stability. The increased nano confined areas inside the polymer matrix where the macromolecular chain mobility is restricted leads to thermal stability enhancement.

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