Journal of Ultrafine Grained and Nanostructured Materials
https://jufgnsm.ut.ac.ir
Vol. 58, No.1, June 2025, pp. 15-24
Print ISSN: 2423-6845 Online ISSN: 2423-6837
DOI: 10.22059/jufgnsm.2025.01.02

The tensile and thermal behavior of polyethylene/silica nanocomposites for high temperature applications produced via injection molding

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Recieved: 5 December 2024; Accepted: 2 February 2025

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ABSTRACT

Polyethylene-silica (PE/SiO_2) nanocomposites have gained significant attention in various fields due to their enhanced properties. Overall, the versatility of polyethylene-silica nanocomposites makes them valuable in advancing technology across multiple sectors. This study tries to examine the role of SiO_2 nano particles on the tensile and thermal behavior of polyethylene (PE). To do so, polyethylene/silica nanocomposites with varying percentages of silica nanoparticles (i.e. 0, 1, 3, 5%, and 10) were produced using a double screw extruder and standard samples were then produced through injection molding. Tensile test, differential scanning callorimetry (DSC) and thermal graviometry (TGA) analysis were done. The results indicated that as the silica content reached 10 wt%, the Young's modulus and tensile strength of pure PE increased from 0.8 MPa and 14.5 MPa to 1.4 GPa and 17.5 MPa, respectively. An increase of approximately 7.5°C in the crystallization temperature was observed in the PE reinforced with 10 wt% silica nanoparticles, as SiO_2 acted as a nucleating agent. The thermal stability of the nanocomposite was increased by the addition of SiO_2 nanoparticles.

Keywords: *Polyethylene, Silica nanoparticles, Tensile behavior, Thermal behavior, Double screw extruder, Injection molding.*

1. Introduction

Polyethylene is significant not only for its suitable physical properties but also for its chemical neutrality.These features, along with low price and good process ability, have led to the use of polyethylene in wide and diverse applications. The physical properties of polyethylene originate from its semi-crystalline nature, and most of its properties are influenced by the combination of its crystalline and non-crystalline regions. But despite its suitable physical properties, the dimensional instability of polyethylene under long-term stress and low softening temperature has caused this polymer to be separated from engineering plastics and used only in short-term applications or applications without critical stresses [1]. Improving the properties of polyethylene (PE) can be accomplished through various methods, including additive blending, copolymerization, and blending with other polymers. Techniques such as crosslinking and the incorporation of nanomaterials can enhance heat resistance, mechanical strength, and overall performance. Additionally, optimizing processing techniques and modifying surfaces can lead to better adhesion, insulation, and tailored characteristics for specific applications. In order to improve the physical and mechanical properties of PE adding some reinforcements to it is very common.

Nanosilica is currently one of the most commonly used amorphous particles among nanoparticles [2]. Silica nanoparticles serve as effective reinforcements for polymers such as polyethylene, polypropylene, and epoxy. They can significantly enhance various properties of composites, including wear and scratch resistance, thermal stability, rheological characteristics, hardness, modulus, and gas solubility. As a result, nanosilica is widely utilized in plastics, rubbers, adhesives, and coatings [3, 4].

Due to the wide applications for silica nanoparticles (fillers), the usage of silica as a reinforcement in polymer nanocomposites is very common. Good thermal stability, excellent mechanical elasticity, low shrinkage, low thermal expansion and low residual stress are the reasons of using silica as reinforcement. Polymer/silica nanocomposites have been used in automobile and packaging industries [2, 4].

The results of the previous works showed that the addition of nanoparticles to polyethylene increased the elastic modulus and in some cases increased its tensile strength. Sahebian et. al. [5] investigated the effect of coated and uncoated calcium carbonate on the fracture toughness of high-density polyethylene-calcium carbonate nanocomposites and showed that adding 10vol% of uncoated calcium carbonate to high-density polyethylene resulted a decrease in the fracture toughness of nanocomposites. They demonstrated that, at the same volume percentage of calcium carbonate, the fracture toughness of uncoated polyethylene-calcium carbonate nanocomposites decreased due to the strong tendency of calcium carbonate particles to agglomerate. But in the presence of stearic acid as a surface coating agent fracture toughness of PE increased. The reason for this improvement is the positive effect of stearic acid to prevent the agglomeration of particles [5]. A. Lazzeri et. al [6] investigated the effect of surfactant (surface active agent) on the physical, mechanical and deformation behavior of high-density polyethylene nanocomposites reinforced with very fine calcium carbonate particles and found that adding 10vol% calcium carbonate to the polymer, causes to increase the Young's modulus and the yield stress of the composites. The addition of stearic acid on the surface of calcium carbonate reduced the Young's modulus and also the yield stress of the composites compared to the composites reinforced with uncoated calcium carbonate [6]. Sezgin ersoy et. al. [7] investigated the morphological, thermal and mechanical properties of high density polyethylene composites reinforced by zinc oxide nanoparticles, magnesium hydroxide and calcium carbonate. The results showed that the addition of calcium carbonate to the polymer matrix reduced the values of elastic modulus, yield stress, tensile strength and elongation at break. A decrease in the elastic modulus was observed simultaneously with the formation of agglomerated particles at high filler percentages. They also attributed this issue to poor adhesion between the filler and the matrix. Based on the results, the melt flow index of the composites also decreased as the filler content increased [7]. J. D. Wu et. al [8] reported a method by coating nano-SiO2 onto the surface of PE fibers via polydopamine (PDA) as a bridge [8]. D. Guo [9] was employed SiO_2 as additives in the formation of polyethylene/SiO_2 hollow fibre composite membranes using the thermally induced phase separation (TIPS) method [9]. Mohammadi [10] et al. investigated the effect of addition of silica nanoparticles to polyethylene on its viscoelastic behavior. They showed that at constant frequency the storage modulus of all materials including PE and its nanocomposites decreased as temperature increased. Also the value of loss modulus increased as the polyethylene and it nanocomposites approached from low temperatures to the glass transition temperature [10]. To the best of our knowledge the most important researches on PE nanocomposites concentrated on the membrane [11-13]. For example the purpose of study of J. Xu et. al. [12] was to reduce the severe shrinkage of the ultra high molecular weight polyethulene (UHMWPE) membrane during low-concentration molding processing. In this study, using SiO_2 inorganic particles as inner reinforced materials and copper fibers as core support bodies significantly improved the structural stability of the membrane [12]. Among the nanoparticles added to polyethylene, modified clay nanoparticles are particularly useful. In contrast, mineral nanoparticles such as silica, titanium, and zirconium have received less attention [14]. For this reason in the current research, the effect of addition of silica nanoparticles to polyethylene on its tensile and thermal behavior has been investigated. Current research has demonstrated the production of polyethylene/silica (PE/SiO_2) nanocomposites using both injection molding and twin-screw extrusion techniques. While these methods have some limitations, such as high initial costs, design constraints, and longer cycle times, they effectively disperse silica nanoparticles within the polyethylene matrix, thereby enhancing the mechanical and thermal properties of the resulting nanocomposite. The injection molding process is particularly beneficial for creating complex geometries with precise dimensions, whereas twin-screw extrusion allows for continuous processing and improved control over homogeneity.

2. Experimental procedure

2.1. Materials

In the current research silica nanoparticles with average size of about 10 nm and density 2.1 g/

cm^3 produced by Nanolin company (China) have been used. The transmission electron microscopy (TEM) image of the nanoparticles can be seen in Figure (1). As seen the morphology of nano silica is almost spherical and the distribution of its size is uniform.

Polyethylene with the trade name HD 7255 is prepared from Maroon petrochemical complex, Iran. Melt Flow Rate (190°C/2.16kg) and density of the used PE are 4 (g/10min) and 0.954 (g/cm^3) respectively.

2.2. Sample preparation

To produce polyethylene/silica nanocomposites, polyethylene granules and silica nanoparticles were weighed, mixed mechanically, and then fed into a double screw extruder operating at a temperature range of 200-230 °C. Afterward the standard samples (ASTM D638) were produced using injection molding. PE nanocomposites reinforced with different weight percentages of silica nanoparticles (i.e. 0, 1, 3, 5 and 10) were produced by Manomet model injection machine (Germany) in a temperature range of 220 to 230 °C. It is worth noting that the maximum content of nano silica in polyethylene (PE) can vary depending on several factors, including the specific application, the processing conditions, and the desired properties of the final material. A. M. Al-Thobity et. al. [15] in 2021 published a paper at which they showed that generally, the incorporation of nanosilica into a polymer can range from a few percent up to around 7% by weight. In the current study the authors try to increase the content of silica using twin-extruder and injection molding of about 10%. The composition and short name of the produced samples are summarized in Table 1.

2.3. Tensile test

Tensile test was performed in accordance with ASTM D638 at cross-head speed of 10 mm/min. For tensile testing, a computer controlled Santam universal testing machine (STM-15, Iran) was used. For each run 5 samples were tested and the average values were reported. The used samples were tested with dimensions of approximately 165 mm in length, 13 mm in width, and 3.2 mm in thickness.

2.4. Thermal behavior

The thermal behavior of the PE and its nanocomposites was carried out using differential scanning calorimetry (DSC) analysis Mettler Toledo (DSC 3, Switzerland). The approximate weight of the samples was about 10 mg. The samples were first heated from room temperature to 200 °C at a rate of 10°C/min, then the samples were cooled from 200 °C to room temperature and heated again up to 200 °C. In order to investigate the thermal stability of the samples thermal gravimetric analysis (TGA) was performed. This test was conducted on 10 mg of the samples using Mettler Toledo (DSC 3, Switzerland). The heating rate was 10°C/min and the sample was heated from ambient temperature up to 600°C.

3. Results and discussion

Table 2 shows the results of tensile tests for pure PE and its nanocomposites. As seen, both Young's modulus and tensile strength of PE increase with increasing silica content. The reason of this variation can be attributed to the fact that silica particle has modulus higher than that of PE. Besides silica particles has significant effect on the free volume of PE and at high silica content PE molecular chains

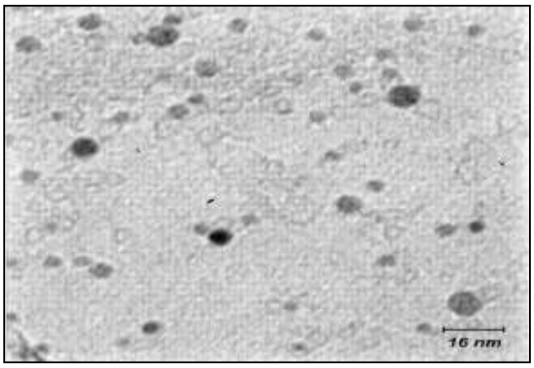


Fig. 1- TEM micrograph of silica nanoparticles (Particles appear in black and gray).

Table 1- The composition and short name of all produced samples

Sample	SiO$_2$ (wt%)
A	0
B	1
C	3
D	5
E	10

do not have enough energy to move and in this condition the chains force to tolerate the external stress. It is clear that when the silica content is more, the more chains will be blocked resulting an increase in the tensile strength of the PE. The reason of reducing tensile strength of composite at content of silica higher than 5wt% can be attributed to the fact that in a nanocomposite material, nanoparticles are meant to enhance mechanical properties by transferring stress from the matrix to the nanoparticles. Agglomerated nanoparticles can inhibit this load transfer, reducing the overall strength of the composite. It is worth noting that the tensile properties of particulate filled composite depend strongly on the several factors including geometry of the reinforcement materials (shape, size, size distribution), particle surface morphology and structural characteristics of the particles, concentration and its concentration distribution in a polymer matrix [14, 16-18].

The thermal behavior of pure PE and its nanocomposites were evaluated by DSC and TGA. Figures (2-a) to (2-c) show thermal behavior of PE, PE/1wt%SiO_2 and PE/10wt% SiO_2 respectively. The starting temperature of crystallization (T_{onset}), melting temperature (T_m), temperature of the exothermic peak of crystallization (T_c), degree of cooling ($\Delta T=T_{onset}-T_c$), melting enthalpy (ΔH_m), enthalpy of crystallization (ΔH_c), and percentage of crystallization or crystallinity (X_c) for the samples are summarized in Tables 3 and 4.

As can be seen in Table 3, the melting point of polyethylene does not show the significant dependency on the reinforcement content implying the compatibility of SiO_2 nanoparticles with the polymer material (polyethylene) unlike the crystallization temperature. This is because SiO_2 acts as nucleating points and in its presence the first crystals are formed around them. In fact the presence of silica nanoparticles can enhance the thermal stability of polyethylene, increasing the temperature at which degradation occurs. However, if the nanoparticles are agglomerated (in this study: sample E), this effect may be diminished due to limited effective surface area and interactions. This result is similar to what proposed by other investigators [19-22].

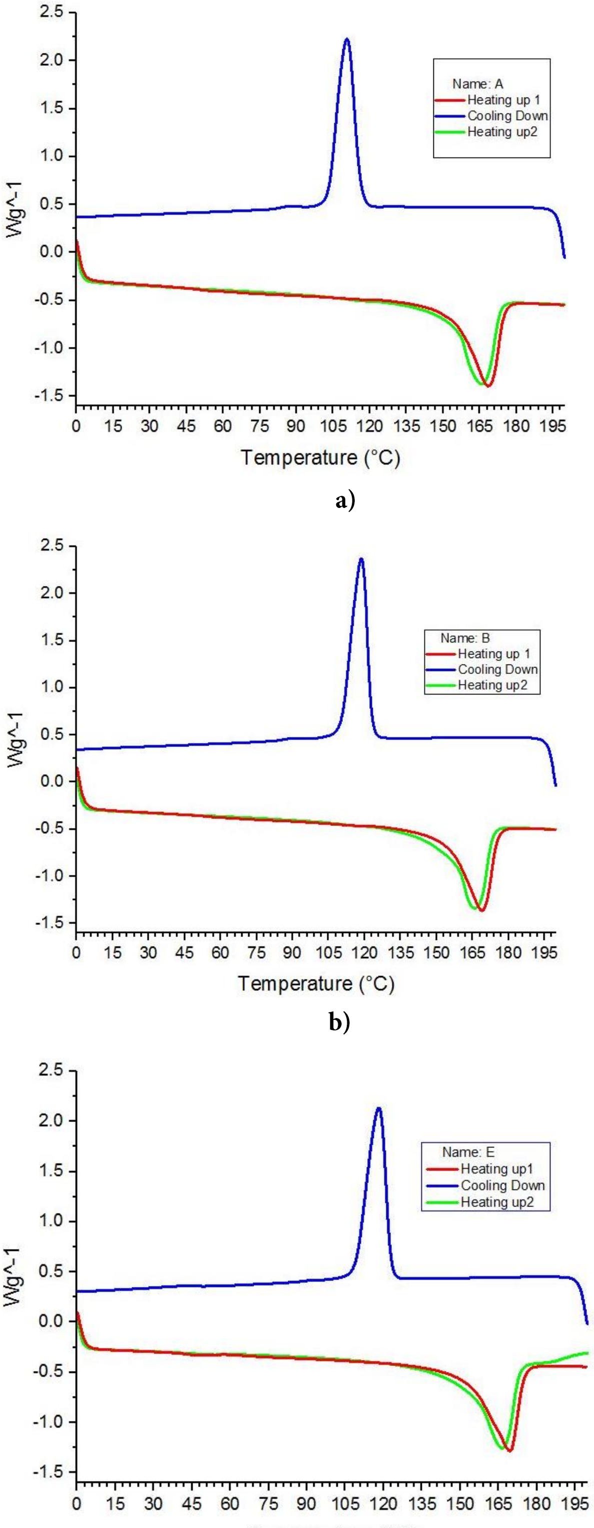
The crystallinity of the samples was calculated using equation 1, where $\Delta H_{Composite}$ is the enthalpy of the analyzed sample and ΔH equals to the

Table 2- Tensile properties of PE and its nanocomposites

Sample	Young's Modulus (GPa)	Tensile Strength (MPa)
A	**0.8**	**14.5**
B	**1.2**	**16.2**
C	**1.3**	**17.8**
D	**1.4**	**18.5**
E	**1.4**	**17.5**

Table 3- The melting and crystallization temperatures of produced samples

Sample	T_m (^oC)	T_c (^oC)
A	**165.7**	**110.6**
B	**165.7**	**118.6**
C	**165.9**	**118.9**
D	**164.5**	**120.3**
E	**166.5**	**118.1**



a)

b)

c)

Fig. 2- DSC test for some produced samples: a) Pure PE, b) PE/1wt%SiO_2 , c) PE/10wt% SiO_2 .

enthalpy value of the polymer sample with 100% crystallization, which is considered to be 292.88 j/g.

$$X(\%) = \Delta H_{\text{Composite}} / \Delta H \times 100 \quad (1)$$

As seen in Table 4 silica nanoparticles can significantly influence the thermal properties of polyethylene. When silica nanoparticles are incorporated into PE, they can affect the enthalpy of melting (ΔH_m) in several ways. Silica nanoparticles can act as nucleating agents during the crystallization of polyethylene. This can lead to a more refined crystalline structure, which can affect the melting behavior of the polymer. A more uniform and fine crystalline structure can often result in a higher melting point and potentially alter the enthalpy of melting. The interaction between the silica nanoparticles and the polyethylene

Table 4- Crystallinity calculated by DSC test

Sample	ΔH_m (mj) Normalized	Crystalinity (%)	T_{onset} (^{O}C)	ΔT
A	**95.11**	**32.47**	**116.4**	**5.8**
B	**94.7**	**32.65**	**123**	**5**
C	**93.13**	**32.78**	**123.3**	**4.4**
D	**94.88**	**34.09**	**124.65**	**4.3**
E	**95.30**	**36.15**	**122.98**	**4.8**

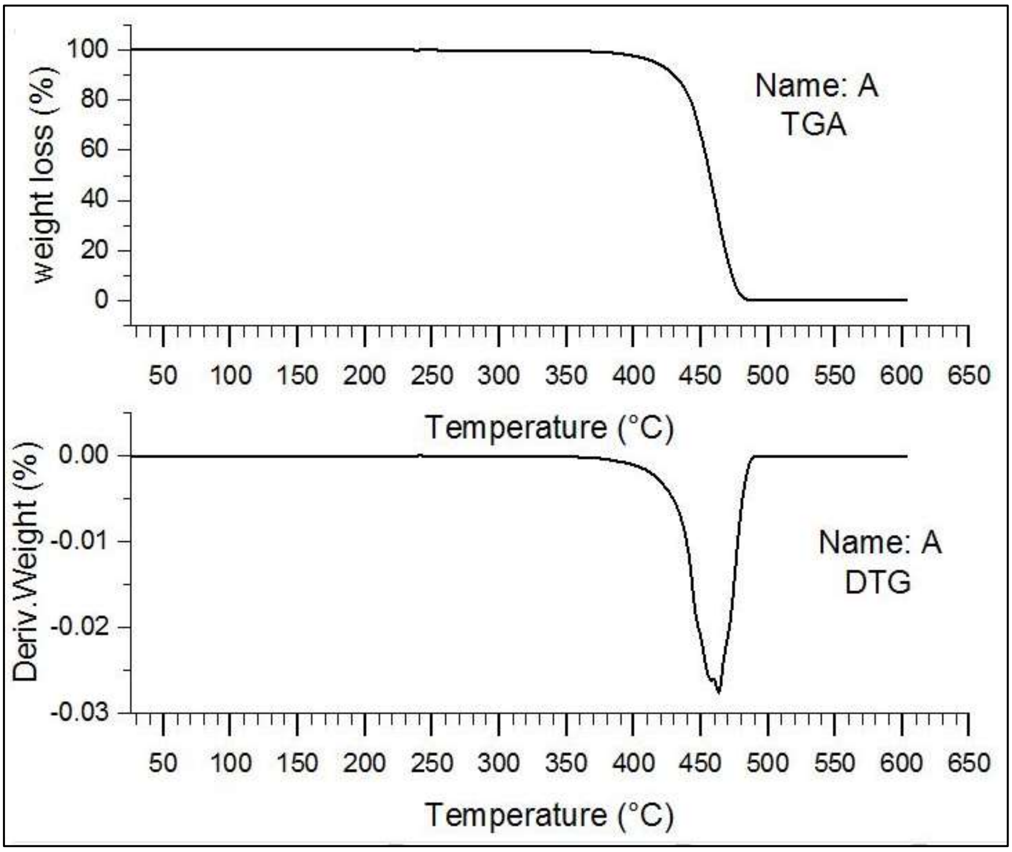


Fig. 3- TGA and DTGA for pure PE.

matrix can modify the energy required to break intermolecular interactions during melting. The presence of nanoparticles may lead to stronger interactions at the interface, affecting the overall energy dynamics during the melting process. Also the addition of silica nanoparticles can improve the thermal conductivity of the composite material. This can lead to more efficient heat transfer during melting, which may influence the measured enthalpy of melting [21-23].

The thermal stability of the samples was evaluated using TGA testing. Based on the results presented in Figure 3, it is evident that the degradation of polyethylene occurs in a single step. To understand the effect of adding SiO_2 nanoparticles on the degradation mechanism and stages of polyethylene, the TGA results for the nanocomposite samples will provide valuable insights. Figure 4 displays the TGA and DTGA diagrams for the PE/10wt%SiO_2 samples. By looking more closely at figures 3 and 4, it can be seen that the presence of silica nanoparticles has caused a serious change in the temperature of polyethylene degradation. The presence of silica nanoparticles can reduce the rate of thermal degradation of polyethylene. This can be attributed to the barrier effect of the silica particles, which can hinder the diffusion of volatile degradation products and oxygen, thereby slowing down the degradation process.

To clarify the role of silica content on the thermal stability of polyethylene (PE) across various temperature ranges, it is essential to examine the TGA and DTGA data in greater detail. Figures 5 and 6 present TGA and DTGA curves for the temperature range of 25-600°C, while Figures 7 and 8 display the curves for the range of 400-500°C. All samples exhibit a single-stage degradation, indicating that the presence of SiO_2 nanoparticles does not significantly affect the degradation process. The TGA derivative illustrates the number of degradation steps; as shown in Figure 8, the DTG diagram for all samples reveals the same steps, confirming that degradation occurs in a single stage. Specifically, the degradation behavior of both pure and nanocomposite PE takes place within the temperature range of 400-500°C. Above 480°C, thermal degradation is observed, albeit in minimal amounts, up to 600°C. The enhanced thermal resistance of PE nanocomposites can be attributed to the high thermal stability of SiO_2. Previous research has indicated that incorporating ceramic particles like SiO_2 can improve the thermal resistance of polymers such as PE [21, 23]. When the neat polymer begins to degrade, heat must concentrate at the locations of the polymer chains, resulting in bond breakage. However, when SiO_2 nanoparticles are present among the polymer

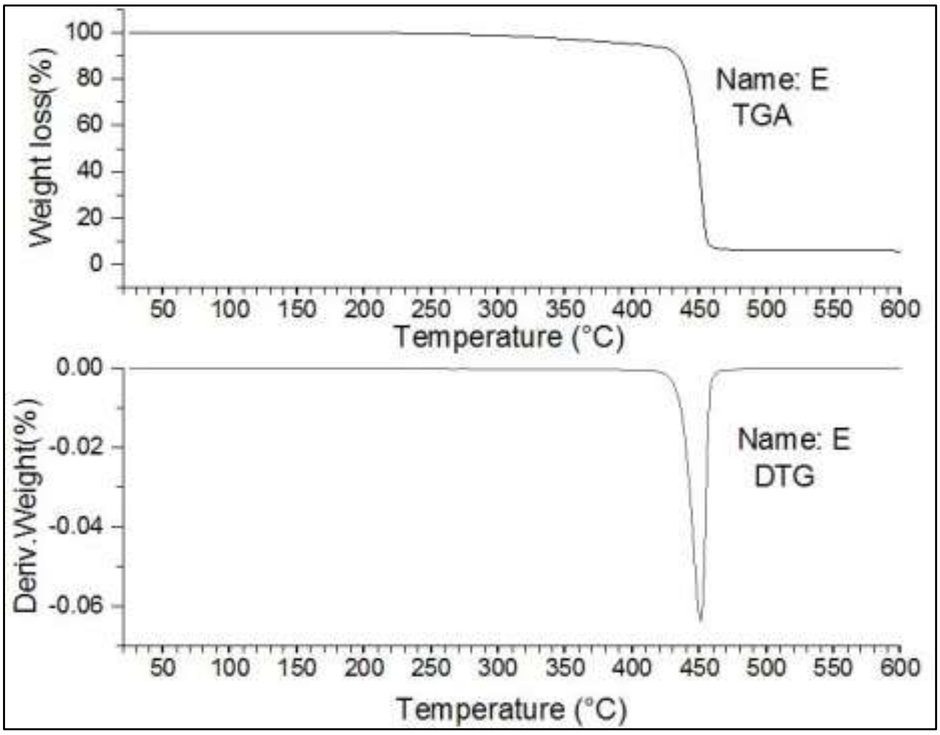


Fig. 4- TGA and DTGA for PE/10wt%SiO_2.

chains, heat is effectively absorbed by the SiO_2, acting as an insulator, which prevents the polymer matrix from experiencing the heat directly. This is because the C_P (heat capacity) of nano SiO_2 is much higher than that of PE.

Briefly the results of current study show that the thermal properties of polyethylene/silica (PE/SiO_2) nanocomposites can be influenced by several parameters. The amount of SiO_2 incorporated into the PE matrix can significantly affect thermal stability and thermal conductivity. Generally, an optimal amount of filler can enhance thermal properties, but excessive amounts may result in agglomeration and reduced performance. The degree of crystallinity in polyethylene affects thermal properties. More crystalline structures often exhibit higher melting temperatures and better thermal stability. It is clear that besides the mentioned parameters the size and shape of the silica nanoparticles play a crucial role. Smaller particles with a high surface area can improve dispersion and interaction with the polymer matrix, enhancing thermal properties. Surface Modification of SiO_2: Functionalizing the silica surface (e.g., with silanes or other coupling agents) can improve the compatibility between the silica and the polyethylene, affecting the thermal stability and conductivity. The molecular weight of the polyethylene can influence its thermal properties. Higher molecular weights typically lead to improved thermal stability.

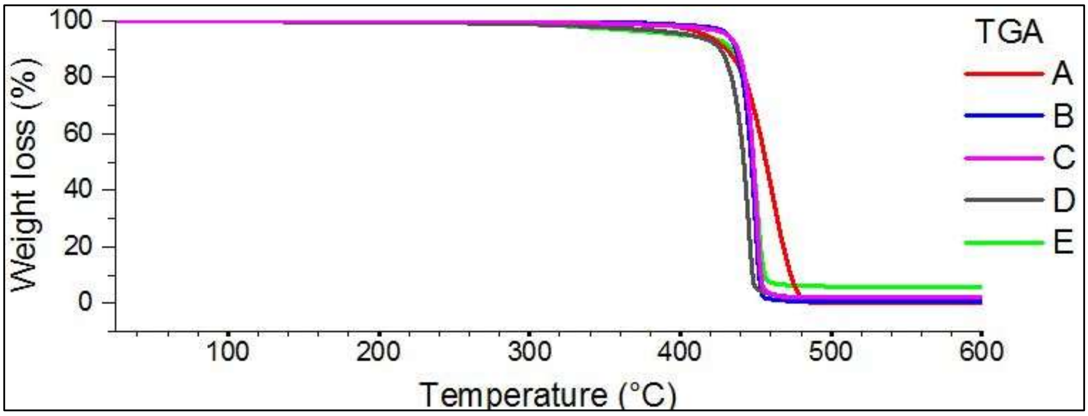


Fig. 5- TGA curves in the range of 25-600 °C.

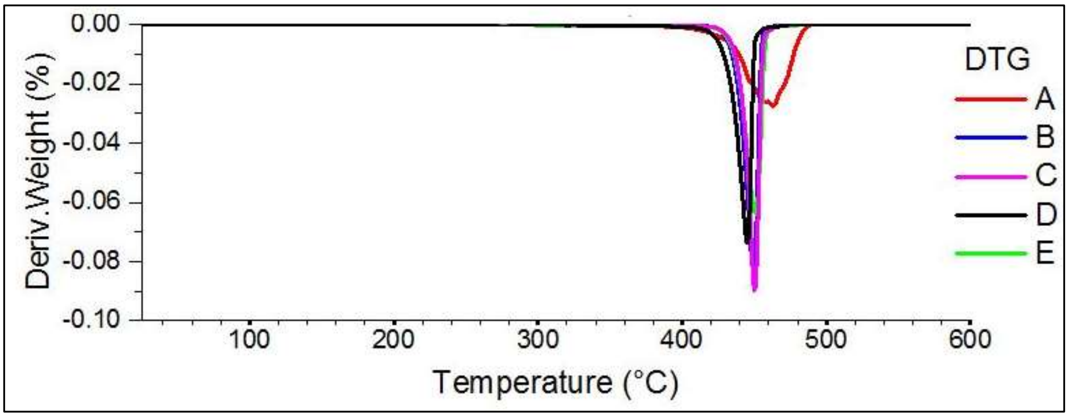


Fig. 6- DTGA curves in the range of 25-600 °C.

4. Conclusions

Polyethylene/silica nanocomposites have attracted considerable attention in various fields because of their improved properties. Their versatility makes them valuable for advancing technology across multiple sectors. In the current research, the effect of addition of silica nanoparticles to polyethylene on its tensile and thermal behavior has been investigated. The results are remarked as follows:

- Both Young's modulus and tensile strength of PE increased with increasing silica content.
- Crystallization temperature of PE increased from 110.6 to above 118 °C as silica content increased from 0 up to 10wt%.
- Melting point of polyethylene did not show significant dependency on the reinforcement content.
- An increase in the thermal resistance of PE observed as silica nanoparticles added to it.

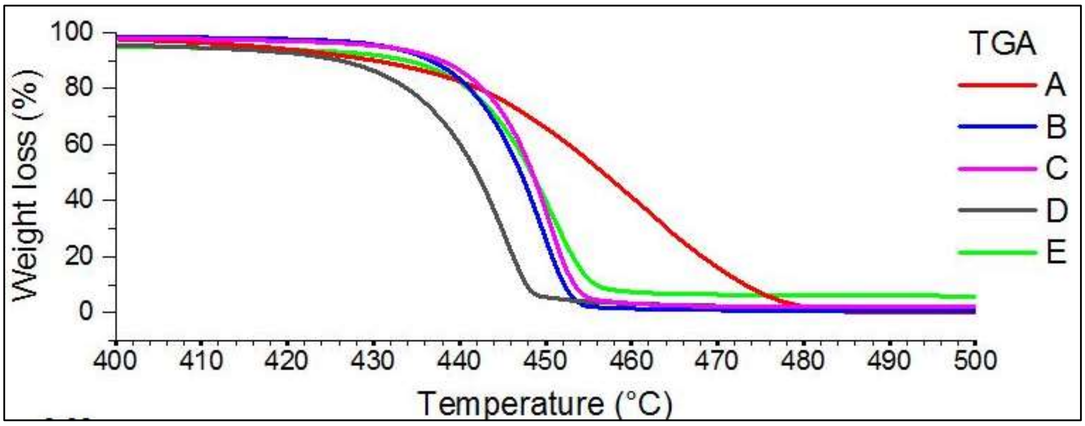


Fig. 7- TGA curves in the range of 400-500 °C.

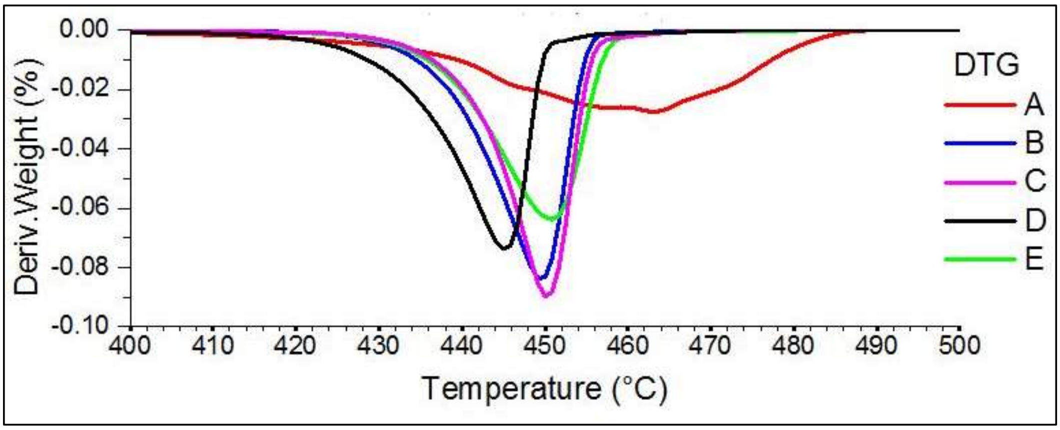


Fig. 8- DTGA curves in the range of 400-500 °C.

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