Thermal Characterization of PS/TiO_2 and HDPE/TiO_2 Nanocomposites: Effects of TiO_2 Concentration on Dispersion and Thermal Stability

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Abstract. This study investigates the influence of TiO_2 nanoparticles on the thermal behavior of polystyrene (PS) and high-density polyethylene (HDPE) nanocomposites. PS/TiO_2 and HDPE/TiO_2 films were prepared using a solution mixing technique followed by hot pressing, and their thermal properties were examined through differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). Incorporation of TiO_2 enhanced the thermal stability of both polymer systems. In HDPE/TiO_2, low nanoparticle concentrations acted as nucleating agents, slightly increasing the melting onset associated with the semi-crystalline nature of HDPE. For PS/TiO_2, the melting temperature (Tm) and glass transition temperature (Tg) increased with nanoparticle loading, indicating restricted chain mobility due to strong interfacial interactions. A reduction in enthalpy of melting (ΔH) and crystallinity (Xc) in both systems confirmed that TiO_2 disrupted polymer crystallinity. TGA results further revealed increased decomposition temperatures for the nanocomposites compared to neat polymers. These findings demonstrate that TiO_2 nanoparticles effectively enhance the thermal resistance and stability of PS and HDPE, making them promising candidates for advanced thermal-demanding applications.

Keywords: Nanocomposites, Polyethylene, Polistrol, Nanoparticles

1. Introduction

The development of advanced polymer nanocomposites is one of the key priorities in modern materials science and technology. Combining the physicochemical properties of polymer matrices with the functional characteristics of nanofillers enables the fabrication of multifunctional materials with improved performance. Such nanocomposites have attracted considerable attention due to their enhanced thermal, mechanical, and structural stability, which make them suitable for diverse applications in electronics, energy systems, biomedical technologies, and insulation materials [1-5]. Metal oxide nanoparticles are of particular interest as nanofillers owing to their high surface-to-volume ratio, tunable surface activity, and strong interaction with polymer chains. Their incorporation into polymers can significantly alter chain mobility, crystallization behavior, and thermal degradation pathways,

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resulting in improved thermal resistance and extended service lifetimes [2-4]. Even at low loading levels, metal oxide nanoparticles can promote more uniform dispersion, create broader interfacial contact, and enhance matrix–filler interactions, leading to superior material properties compared to conventional micro-filled polymers [3-6]. Polystyrene (PS) and high-density polyethylene (HDPE) are widely used thermoplastic polymers with hydrophobic, non-polar characteristics. Improving their thermal and structural properties is essential for applications requiring enhanced heat resistance and long-term stability. Titanium dioxide (TiO_2) nanoparticles have been reported as effective inorganic fillers for enhancing thermal stability, restricting chain mobility, and modifying crystallinity in polymer systems [7-14]. In this work, PS/TiO_2 and HDPE/TiO_2 nanocomposites were fabricated using a solution-mixing technique followed by hot pressing. TiO_2 nanoparticles were incorporated into the polymers at 3, 5, and 10 wt% concentrations. The thermal properties of the prepared nanocomposites were systematically investigated using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) to evaluate the influence of TiO_2 nanoparticles on the thermal behavior and stability of PS and HDPE

2. Materials and Methods

2.1. Materials

HDPE polyethylene granules (SOCAR, 'Azerikimya' Production Union 'Etilen-Polyethylene' plant, 15803-020),by a density of 0.92 g/cm^3 , a melting temperature range of 150°C, CCl_4 organic solvent (Code 141245, 99.5%, CAS No. 56-23-5, Common Chemistry-P.L.C.), titanium oxide nanoparticle (TiO_2), rutile (99,9%, 30-50nm, T689, Hongwu International Group, Ltd, China) were used in the study. All chemicals were used as received without undergoing purification. Polystyrene (PS) (CAS number 9002-86-2) was characterized by a density of 1.04 g/cm^3, a melting temperature range of 150–220°C, a flash point of 625°C, an ignition temperature of 500°C, and an auto-ignition temperature exceeding 1100°C. Tetrahydrofuran (THF) with product code 143537 was also used as received.

2.2. Preparation of Polymer Nanocomposites

Polymer nanocomposite materials were synthesized by a combination of two methods, namely solution mixing and hot pressing process. First, high-density polyethylene was dissolved in its organic solvent carbon tetrachloride (CCl_4), and polystyrene was dissolved in tetrahydrofuran (THF). Titanium oxide nanoparticles at different concentrations of 3%, 5% and 10% were accurately weighed and added to HDPE-CCl_4 and PS-THF solutions. The mixture was vigorously stirred for 8 hours to ensure complete homogeneity of TiO2 nanoparticles within the solution. Then, the resulting mixture was poured into a Petri dish and air-dried for 24 hours. To completely remove the solvent from the polymer matrix, the nanocomposites were dried in a vacuum oven at room temperature for 2 hours. Then thin layers of the nanocomposites were prepared by hot pressing at 160°C - 180°C and 10 MPa. After hot pressing, the composition was cooled by immersing in water at room temperature.

2.3. Instrumentation

Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were conducted in the temperature range T = 20–550°C using an STA3000 Synchronous Thermal Analyzer at a heating rate of 20°C/min. Ceramic (Ce) cuvettes were used during the experiment. The experiment was conducted in a nitrogen (N_2) atmosphere. Samples were heated from 20°C to 550°C at a rate of 20°C/min. Each sample weighed approximately 85–87 mg. This temperature range was chosen to capture the significant thermal transitions in polystyrene (PS) and its nanocomposites, offering insights into polymer matrix's stability near its degradation temperature. The selected heating rate balanced resolution and efficiency, ensuring clear observation of thermal events while minimizing thermal lag. The degree of crystallinity of the HDPE/TiO_2 and PS/TiO_2 nanocomposites was calculated from the melting enthalpy, which reflects the proportion of the crystalline phase in the structure, using Equation:

$$X_C = \frac{\Delta H_m}{\Delta H_{lit}} \cdot 100\%$$

where ΔH_m is the melting enthalpy of the sample, and ΔH_{lit} is the tabulated value for the melting enthalpy of a 100% crystalline polymer.

3. Results and Discussion

3.1. Differential Scanning Calorimetry analysis

The thermal properties of high-density polyethylene (HDPE) and polystyrene (PS) polymer matrices modified with surface TiO_2 nanoparticles were investigated using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). TGA is employed to monitor the thermal degradation behavior of the composites by heating the sample to elevated temperatures, while DSC is used to measure the heat flow associated with phase transitions.

The thermal properties of HDPE/TiO_2 and PS/TiO_2-based nanocomposites are summarized in Tables 1 and 2. From the DSC curves (Fig. 1–2), it is observed that the incorporation of titanium dioxide (TiO_2) nanoparticles into HDPE and PS matrices enhances their thermal stability and allows the detection of the glass transition temperature (Tg) in both polymer nanocomposites. Fully crystalline polymers do not exhibit a glass transition, as their structure remains intact up to the melting point. Since polyethylene is a semi-crystalline polymer, a glass transition temperature is detectable in its DSC curve. It is well established that at Tg, polymers transition from a rigid to a more flexible and elastic state, which increases the mobility of polymer chains. Fig. 1 and Fig. 2 indicate that HDPE-based nanocomposites begin to lose their solid state at approximately 52°C, whereas PS-based nanocomposites start this transition at 65.8°C.

It should be noted that all DSC curves of the samples display a single endothermic peak upon heating, which corresponds to the melting of the crystalline phase in HDPE and PS. Nanocomposite samples, including HDPE/3%TiO_2 and

PS/TiO_2 with 3%, 5%, and 10% TiO_2, exhibit higher melting temperatures compared to the pure polymers. In polyethylene, increasing TiO_2 content to 5% and 10% by mass slightly decreases the polymer's melting temperature. This minor reduction in melting temperature can be attributed to the partial shortening of chain lengths and increased mobility of polymer molecules. The observed decrease is small and is not expected to cause significant changes in the physical properties of polyethylene. This behavior can also be explained by the distribution of nanoparticles throughout the matrix and their potential role as heterogeneous nucleation sites.

Taking the melting enthalpy of PE crystals as 293 J/g [8] as a reference, the degree of crystallinity of the polymer in nanocomposites at high filler contents is 46%. For PS-based nanocomposites, the polymer crystallinity reaches 60%.

Table 1. DSC Results of HDPE/TiO_2 and PS/TiO_2-Based Nanocomposites

Sample	Glass trans.temp., Tg, °C	Melt. temp., Tm, °C	Crystal. temp., Tc, °C	Crystal. entha., ΔH, J/g	Melt. entha., ΔH, J/g	Degree of crys-tal.,%
HDPE	50.95	106.82	92.0	124.35	139.47	47.6
HDPE/3%TiO_2	53.25	109.65	90.6	132.33	137.85	47.04
HDPE/5%TiO_2	51.8	106.3	92.7	131.72	136.64	46.6
HDPE/10%TiO_2	51.6	106.5	92.2	129.65	133.76	45.65
PS	-	405.45	-	-	35.46	66.9
PS/3%TiO_2	74.95	419.74	-	-	33.85	63.8
PS/5%TiO_2	67.5	425.13	-	-	32.35	61.0
PS/10%TiO_2	54.94	445.94	-	-	29.64	55.9

The melting enthalpy of polymer composites generally decreases with increasing TiO_2 content. In our study, a decrease in melting enthalpy was observed in both polymer nanocomposites. Additionally, the incorporation of TiO_2 into the PS/TiO_2 nanocomposite reduced the polymer fraction, resulting in a lower melting enthalpy, and no crystallization was detected (Fig. 2). The DSC curve of the HDPE/3%TiO_2 nanocomposite (Fig. 1b) shows that although the melting temperature slightly increases with 3 wt% TiO_2, both the melting enthalpy and the degree of crystallinity decrease (Table 1). The endothermic peaks observed in the DSC curves (Fig.1a–b) correspond to the melting of both the original polymer crystals and those formed during cold crystallization. During the cooling process, unlike PS/TiO_2 nanocomposites, HDPE/TiO_2 exhibits crystallization. As shown in Fig. 1, with increasing temperature, the rate of heat flow increases, and for HDPE-based HDPE/TiO_2 nanocomposites, the maximum melting occurs at 109.65°C as an endothermic peak. Subsequently, the process releases energy sharply from the crystallization temperature peak at 92.7°C to completion, resulting in an exothermic process. This indicates that the polymer nanocomposite molecules reorganize into their components. During the exothermic process, the macromolecules of HDPE/TiO_2 can crystallize due to molecular movements induced by heat flow. Consequently, the intensity of heat transitions associated with the amorphous fraction of the polymer decreases during cooling (Fig. 1b). The average total energy consumed for the

endothermic process between the onset and completion of melting was 367.25 mJ, whereas the energy released during the exothermic process was 123.31 mJ.

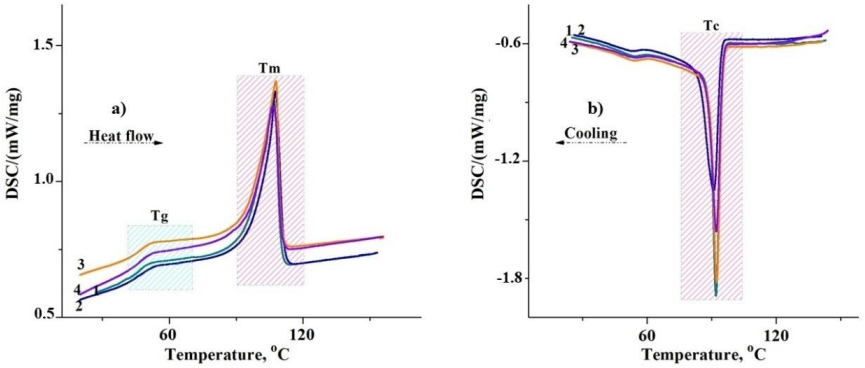

Fig. 1. DSC spectra melting and crystallization curves of HDPE - based HDPE/TiO_2 polymer nanocomposites: 1. Pure HDPE; 2. HDPE/3%TiO_2; 3. HDPE/5%TiO_2; 4. HDPE/10%TiO_2

Our study demonstrates that TiO_2 nanoparticles act as nucleating agents within the polystyrene matrix, promoting the formation of crystalline structures in PS. Moreover, unlike polyethylene-based nanocomposites, an increase in TiO_2 concentration in PS/TiO_2 nanocomposites leads to a decrease in Tg. This behavior is associated with changes in the mobility of PS polymer chains due to interactions between the titanium oxide nanoparticles.

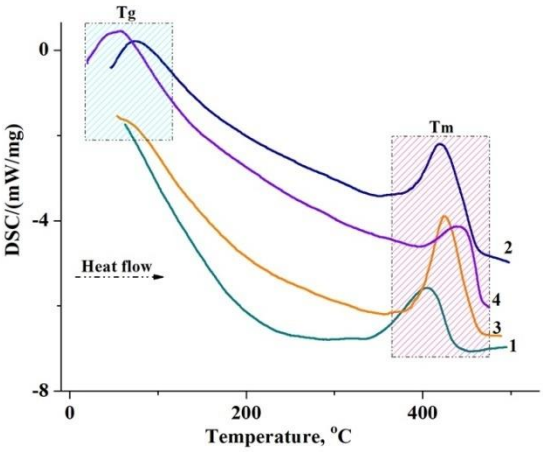

Fig. 2. DSC spectra melting curves of PS - based PS/TiO_2 polymer nanocomposites: 1. Pure PS; 2. PS/3%TiO_2; 3. PS/5%TiO_2; 4. PS/10%TiO_2

From the DSC curves, it is evident that the incorporation of stabilized TiO_2 metal oxide nanoparticles positively influences the thermal properties of both high-density

polyethylene and polystyrene-based polymer nanocomposites. In non-polar HDPE nanocomposites, the crystallization observed during cooling results from the formation of heterogeneous nucleation centers at the polymer-matrix interface induced by the TiO_2 nanoparticles. These centers also facilitate the formation of fine spherulitic structures during crystallization by promoting the development of new nucleation sites within the nanocomposite.

Consequently, an improvement in the thermal properties of HDPE/TiO_2 nanocomposites is observed.

3.2. Thermogravimetric analysis

Fig. 3 shows the thermogravimetric analysis (TGA) curves of high-density polyethylene (a) and polystyrene (b)-based polymer nanocomposites. TGA measurements were conducted by heating the samples from 20°C to 600°C at a rate of 20°C/min. The thermal stability of the samples was evaluated based on the decomposition temperatures corresponding to 3%, 5%, and 10% weight loss, as well as the half-decomposition temperature and the temperature at complete degradation. The results are summarized in Table 2. For pure HDPE, continuous thermo-oxidative degradation occurs starting from 361.54°C and continues up to 510.61°C, resulting in a total mass loss of 98.2%.

As seen in Fig. 3a, the thermo-oxidative degradation temperature of HDPE/TiO_2 nanocomposites, containing 3 wt% titanium oxide nanoparticles, shifts to higher temperatures, reaching 395.16°C. The experimental results indicate that, compared to polystyrene (PS), HDPE exhibits a stronger interaction with titanium dioxide nanoparticles at the microstructural level.

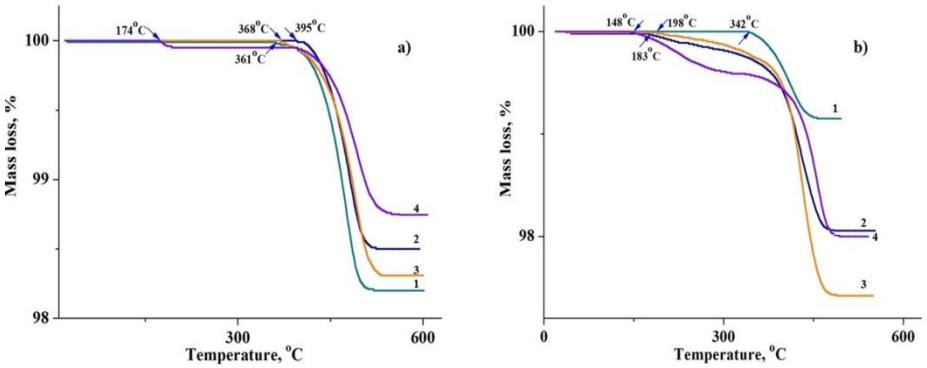

Fig. 3. TGA spectra of HDPE - based HDPE/TiO_2 (a) and PS - based PS/TiO_2 (b) polymer nanocomposites

Modification of HDPE with TiO_2 nanoparticles enhances the thermal stability and thermo-oxidative degradation behavior of the nanocomposite. Furthermore, an increase is observed in all thermo-oxidative decomposition parameters of the HDPE/TiO_2 nanocomposite.

As shown in Table 2, for PS/TiO_2 nanocomposites prepared with 5 wt%TiO_2, the main characteristic thermal stability remains at 198.8°C. Fig. 3b shows that although PS and TiO_2 interact well at the microstructural level, the resulting nanocomposite becomes brittle upon incorporation of titanium oxide nanoparticles, with decomposition beginning at 148 °C. In contrast, incorporating 3–5 wt% TiO_2 nanoparticles into the HDPE matrix results in enhanced thermal properties of the resulting nanocomposites. The thermo-oxidative degradation of HDPE/5–10 wt%TiO_2 nanocomposites shifts to higher temperatures, ranging from 368.08°C to 395.16°C, with continuous mass loss observed up to 523.48–549.9°C, after which the mass loss ceases. The onset temperature of thermo-oxidative degradation in HDPE with 10 wt%TiO_2 is slightly lower. These results indicate that the incorporation of TiO_2 nanoparticles into the HDPE matrix improves the polymer's thermal stability.

Table 2. TGA Results of HDPE/TiO_2 and PS/TiO_2-Based Nanocomposites

Sample	Initial Decomposition Temperature (°C)	Half Decomposition Temperature (Mass Loss, °C)	Final Decomposition Temperature (°C)	Residual mass (mg)
HDPE	361.54	454.14	510.61	1.8
HDPE/3%TiO_2	395.16	469.56	523.48	1.5
HDPE/5%TiO_2	368.08	468.82	554.22	1.68
HDPE/10%TiO_2	174.36	475.06	549.9	1.24
PS	342.14	368.34	458.98	1
PS/3%TiO_2	183.17	366.47	487.59	1.7
PS/5%TiO_2	198.8	387.86	483.74	2.2
PS/10%TiO_2	148.85	315.61	500.31	1.8

As seen from the TGA curves (Fig. 3b), the onset of thermo-oxidative degradation in PS occurs at 342.14°C. When TiO_2 nanoparticles are added to the PS matrix at 3–10 wt%, the onset degradation temperature shifts to lower temperatures, ranging from 142.85°C to 187.8°C. This indicates that the incorporation of TiO_2 nanoparticles reduces the thermal stability of PS/TiO_2 nanocomposites. The difference in thermal behavior between HDPE/TiO_2 and PS/TiO_2 nanocomposites can be attributed to the formation of a denser and more ordered nanocomposite structure in HDPE-based materials.

4. Conclusion

A comparative analysis of the thermogravimetric properties of polymer nanocomposites containing stabilized TiO_2 metal oxide nanoparticles in both high-density polyethylene and polystyrene matrices indicates that HDPE/TiO_2 nanocomposites exhibit superior thermal stability compared to PS/TiO_2 nanocomposites. This difference can be attributed to the formation of heterogeneous nucleation centers at the polymer–matrix interface in HDPE, induced by TiO_2 nanoparticles. These centers further promote the generation of new nucleation sites within the nanocomposite, resulting in enhanced thermogravimetric properties. In

PS/TiO_2 composites, the melting temperature increases with increasing TiO_2 nanoparticle concentration. The interaction between PS polymer chains and the surfaces of TiO_2 nanoparticles restricts chain mobility, leading to an increase in the glass transition temperature (Tg).

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