Mechanical and Thermal Properties of PP/HDPE Blends Reinforced with ZnO Nanoparticles for Industrial Applications

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ABSTRACT

In this work, a polymeric blend of polypropylene (PP) and high-density polyethylene (HDPE) was prepared with different weight percentages. Zinc oxide nanoparticles (ZnO) were added to the 90/10 and 80/20 blends with different weight ratios (1%, 2%, and 3%) to study their effect on both the mechanical and thermal properties of the PP/HDPE blends. A twin-screw extruder was used for the preparation of polymeric blends and their composites. Mechanical properties (tensile properties and hardness) were studied. Thermal properties using Differential Scanning Calorimetry (DSC) were investigated. Fourier transform infrared (FTIR) was used to predict the change in chemical structure. Results for PP/HDPE blends show that both tensile strength and hardness decrease as the amount of HDPE increases due to immiscibility, and these properties are improved by the addition of ZnO nanoparticles. Thermal properties from DSC show that the melting temperature Tm, crystallization temperature Tc were improved by the ZnO addition, and the degree of crystallinity improved only for the 90/10 blend. FTIR shows that there is only a physical interaction, not a chemical one.

Keywords: *PP, HDPE, Blend, ZnO nanoparticles.*

1. INTRODUCTION

Over the past few decades, research on polymers and polymer blends has had a significant impact on both academia and industry. These materials have enormous promise as a tool for developing novel applications [1]–[3]. The development of novel polymers is now thought to be more expensive than blending existing polymers. By combining two or more polymers with distinct molecular properties, materials with superior end-use properties can be created [4], [5].

Polypropylene (PP) is a common commodity polymer with adequate mechanical properties, transparency, acceptable heat resistance, and a reasonable barrier to moisture; nevertheless, its applications are constrained by its lack of flexibility and poor barrier to oxygen [6]. High-density polyethylene (HDPE), a thermoplastic that shares similarities with polypropylene (PP), is commonly used in combination with PP due to its exceptional toughness and ductility [7]. Since polyethylene and polypropylene are two of the most widely used thermoplastics, their combination has drawn a lot of attention. In addition to the excellent price-performance ratio [8], the versatility of these materials and the wide range of possible modifications are other factors to consider.[8].

Due to the enormous improvements in their physical and chemical properties over matrix polymers, polymer nano composites have gained more and more attention in recent years. There has been a lot of research done on how nanoparticles affect these characteristics.

According to Yerlesen and Taşdemir [9], the mechanical characteristics can be significantly improved by adding just a few percent by weight of nanoparticles. The mechanical properties of the blend are impacted by this immiscibility; hence, various compatibilization techniques have been researched to enhance the blends' properties. Copolymer, reactive polymer, and/or co-solvent additions have historically been used to make immiscible polymer mixtures compatible. However, inorganic nanofillers have recently been discovered to be widely used to increase specific properties as well as play a substantial part in the compatibilization of immiscible polymer blends [10], [11]. According to Salih and Abdalsalam [12], the type of filler, the size and shape of the filler particle, and the filler's content all affect the degree of property augmentation. Due to their biocompatibility and lack of toxicity to human cells, ZnO nanoparticles are potential inorganic fillers and have been widely used in a variety of fields, including sunscreens, paints, and coatings in energy and environmental applications [13]. Strong antibacterial characteristics and high specific surface area to volume ratios are also displayed by ZnO nanoparticles (in mixtures with organic chemicals) [14].

This work involved the preparation of polymeric blend composites using a twin-screw extruder, combining PP/HDPE with ZnO nanoparticles. The objective was to examine the effect of ZnO nanoparticles on the mechanical and thermal properties of 90/10 and 80/20 PP/HDPE blends.

2. MATERIAL AND METHODS
2.1. Materials

The PP type 575p and HDPE type 952 were acquired from Sabic. The properties of these materials are presented in Table 1. Additionally, ZnO nanoparticles with a particle size ranging from 20 to 90 nm were obtained from Dashinou Nanotechnology/China. The properties of these nanoparticles are found in Table 2.

Table 1: The properties of PP and HDPE.

PP properties		HDPE properties	
Property	Data	Property	Data
Density	0.91-0.94 g/cm³	Density	0.95 g/cm³
MFR	10 g/10min	MFR	0.05 g/10min
Melt temperature	160 °C	Melt temperature	130 °C

Table 2: Properties of ZnO nanoparticles.

Property	Data
Density	5.606 g/cm
Melting point	1974 °C
Solubility in water	17.8 °C˙

2.2. Preparation of PP/HDPE blends and PP/HDPE/ZnO composites

The polymeric blends and their composites were blended using a twin-screw extrusion machine. Before the mixing process, the materials (PP and HDPE) were dried at 60 °C using a vacuum oven to get rid of moisture. To prepare PP/HDPE blends, the PP and HDPE were melted and mixed at a temperature of 175 °C, using a screw speed of 25 revolutions per minute. To make the PP/HDPE/ZnO composites, the ZnO nanoparticles were mixed with acetone using ultrasonic waves for 10 minutes. Then, they were added to the PP/HDPE pellets and mixed with a mechanical mixer for 3 minutes. After this stage, the PP/HDPE/ZnO mixture was blended using a twin-screw extruder at 175 °C and 25 rev/min. After extrusion, all the prepared materials were immediately transferred between two rolling wheels to create plastic sheets, and these sheets were compressed using a thermal press at 75 °C. The sheets were then cut using a CNC laser cutter in accordance with ASTM-D to create various forms that were used for various tests (tensile and impact). Table 3 shows the compositions of polymeric blends and their composites.

Table 3: The composition of PP/HDPE blends and their composites.

PP (wt.%)	HDPE (wt.%)	ZnO (wt.%)
100	0	-
90	10	1
		2
		3
80	20	1
		2
		3
70	30	-
60	40	-
50	50	-
0	100	-

2.3. Materials Characterization

The mechanical tests were performed according to the standard testing methods. The tensile strength of polymer blends and their composites was characterized using the WDW-5E universal testing machine with a strain rate of 10 mm/min according to ASTM-D 638IV. A hardness test was performed using a Shore D TH 210 FJ hardness tester according to ASTM-D 2240. For all mechanical tests, three samples were tested for each test, and the average of these values was taken. DSC type TA-60ws was used to determine the thermal properties (Tm, ΔH, Tc, and Xc) of the polymer blends and their composites. The samples passed through a temperature increase from 25°C to 250°C, followed by a temperature decrease from 250°C to 25°C. The heating and cooling process occurred at a rate of 10 °C per minute.

The experiment was conducted in an inert environment free of reactive gases. The degree of crystallinity of the samples was determined using the following equation [15],[16]:

$$Xc = (\Delta Hm / \Delta Ho * Wf) * 100\% \ldots\ldots\ldots\ldots(1)$$

Where: ΔH_m: melting enthalpy of sample determined from DSC; ΔH_o: melting enthalpy of fully crystalline PP, which is 209 J/g [15], [16], and for PE is 293 J/g[17], [18], W_f: weight fraction of PP in the polymeric blends.
FTIR was used to analyze the changes in chemical structure for polymer blends and their composites.

3. RESULTS AND DISCUSSION

3.1. Tensile Properties Results

Figure 1 shows the tensile strength of PP/HDPE blends. It is shown that the tensile strength decreases as the amount of HDPE increases. It was found that the tensile strength decreased from 19 MPa to 7 MPa as the HDPE content increased from 10 to 50% wt.%. In addition, it is found in Figure 2 that the elastic modulus decreased as the amount of HDPE increased. The elastic modulus decreased from 0.32 GPa to 0.13 GPa as the HDPE content increased from 10 to 50% wt.%. In figure 3, it is found that the elongation at break increased as the amount of HDPE increased. It is found that the elongation at break increases from 16% to 25.5% as the amount of HDPE increases from 10 to 50 wt.%. These results are due to the poor miscibility and compatibility and also due to the lower properties of PE when compared to PP. These results are in agreement with [19], [20], which state that the addition of PE polymer to PP causes a reduction in tensile properties due to the higher properties of PP compared to PP. They are also due to the difference in material flexibility between PP and PE that is caused by the presence of the CH_3 group in PP and the H group in PE, which reflect on its mechanical properties.
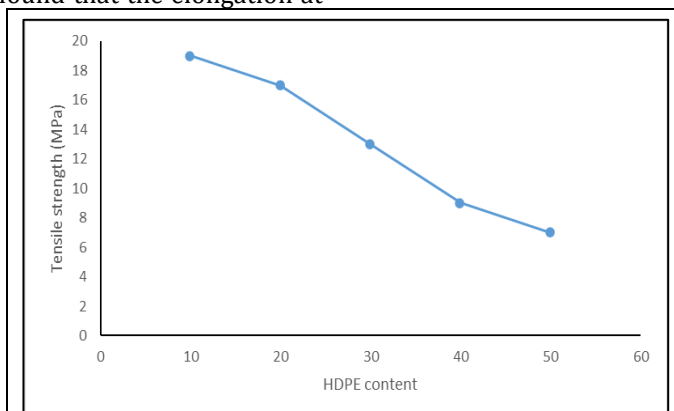

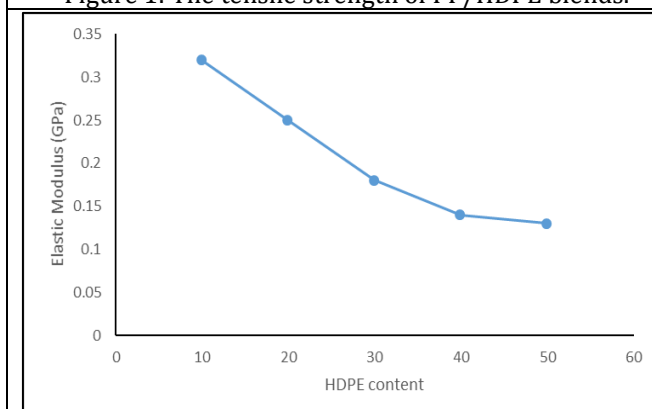Figure 1: The tensile strength of PP/HDPE blends.

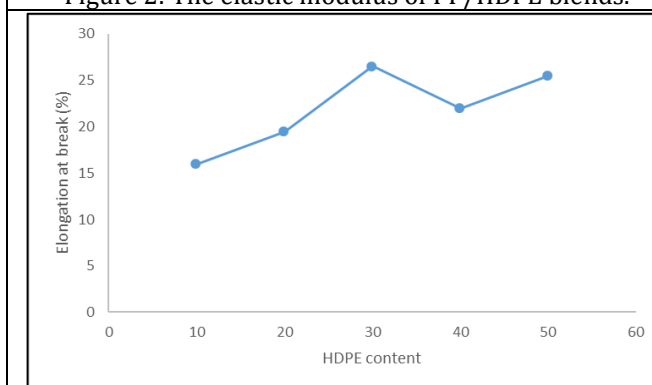Figure 2: The elastic modulus of PP/HDPE blends.

Figure 3: The elongation at break of PP/HDPE blends.

Figures 4 to 6 show the tensile properties of PP/HDPE blends at 90/10 and 80/20 with the addition of ZnO nanoparticles. Figure 4 shows that the addition of ZnO nanoparticles increases the tensile strength of both 90/10 and 80/20 blends. It was found that adding ZnO raises the tensile strength from 19 MPa to 20 MPa as the amount of ZnO nanoparticles goes from 1% wt. to 3% wt. For the 80/20 blends, adding the same amount of ZnO raises the tensile strength from 17 MPa to 20 MPa. In addition, it is found that the highest tensile strength was achieved at 2% wt of ZnO nanoparticles, and it is found that the 80/20 blends have higher strength than the 90/10 blends. Figure 5 demonstrates that the increase in ZnO content for both blends (90/10 and 80/20) increased the elastic modulus. Figure 6 shows the elongation at break for both blends (90/10 and 80/20). It is found that the elongation at break has improved as the amount of ZnO increased from 1 to 3% wt. For the 90/10 blend, it is found that the elongation

increased from 16% at 0 wt. ZnO to 18.7%, 19.5%, and 17.6% at (1, 2, and 3% wt. ZnO), while for the 80/20 blend, it is found that the elongation increased from 19.5% at 0 wt. ZnO to 19.7%, 23%, and 18.5% at (1, 2, and 3% wt. ZnO). These results are due to the higher properties of ZnO particles, which fill the gaps between the polymeric chains and thus increase stiffness and make the blends have higher tensile properties. These results are in good agreement with [5], [21], [22], which state that the addition of nanoparticles to the polymer causes an increase in the polymer stiffness by filling the gaps between the polymer chains and thus restricting the chain movement and making the polymer more stiff even when a soft polymer is added, and this improvement also depends on the distribution of nanoparticles (low-content blends of 1% and 2% have better distribution than the higher-content blends of 3%, which tend to agglomerate).
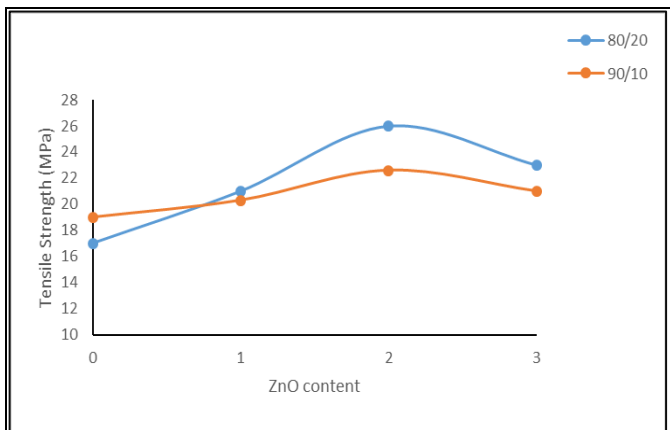

Figure 4: The tensile strength of PP/HDPE blends with ZnO nanoparticles.
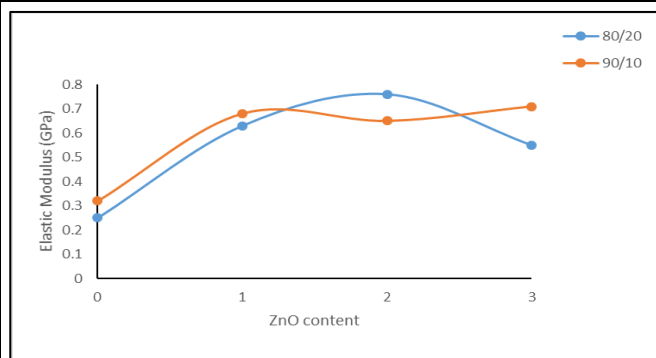

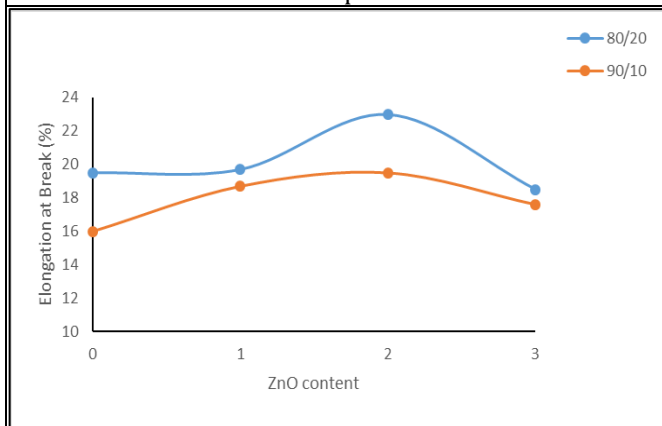Figure 5: The elastic modulus of PP/HDPE blends with ZnO nanoparticles.

Figure 6: The Elongation at break of PP/HDPE blends with ZnO nanoparticles.

3.2. Hardness test Results

Figure 7 shows the Shore D hardness for PP/HDPE blends and their composites with ZnO nanoparticles. From figure 7A, it is found that the hardness decreased as the amount of HDPE increased. The hardness decreased from 65 shore D for pure PP to 58, 55, 56, 50.6, and 55.8 shore D as the amount of HDPE increased from 10 to 50% wt. Figure 7B demonstrates that the addition of ZnO nanoparticles increased the hardness for both 90/10 and 80/20 blends. For the 90/10 blend, it was found that the hardness increased from 58 shore D to 62.6, 60.4, and 59.8 shore D as the amount of ZnO increased from 0 to 3%. In addition, for the 80/20 blend, the hardness increased from 55 shore D to 58.4, 61.3, and 56.7 shore D as the amount of ZnO increased from 0 to 3% wt. These results are attributed to the higher hardness of ZnO and also to the fact that ZnO fills the spaces between the chains, which make the material resist the force applied to the sample surface. These results are in agreement with [12], [21]. They state that hardness is a surface property that depends on the homogeneity and smoothness of the sample's surface (the better the homogeneity, the smoother the surface, and thus the higher the hardness).
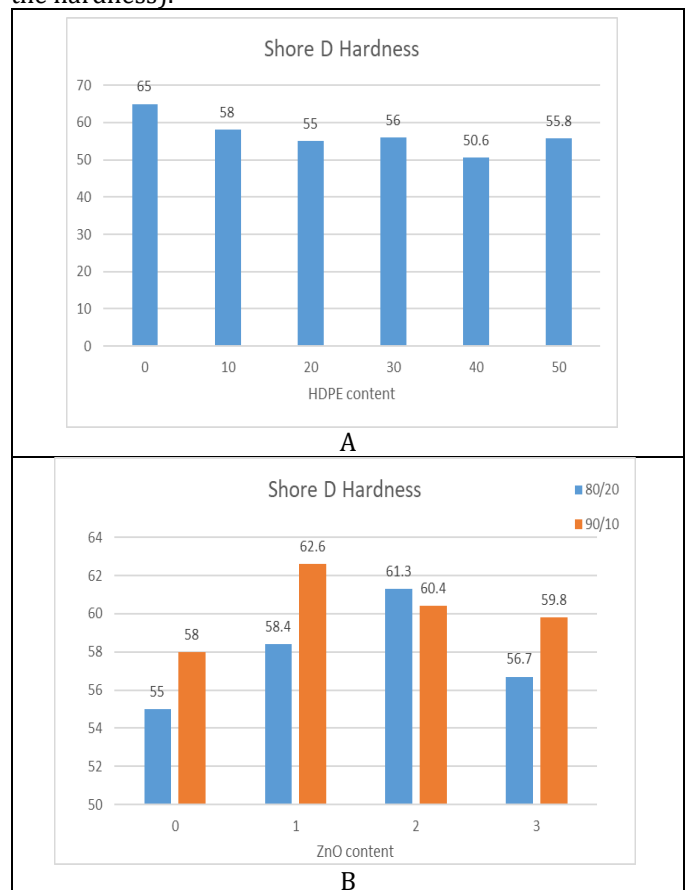

A

B

Figure 7: Shore D hardness of PP/HDPE blends without (A) and with (B) ZnO nanoparticles.

3.3. Thermal Properties

The thermal properties such as the melting temperature T_m, melting enthalpy ΔH_m, crystallization temperature T_c, and degree of crystallinity χ_c for PP/HDPE blends and PP/HDPE/ZnO composites were investigated, as shown by Figure 8. It is shown that the 90/10 and 80/20 PP/HDPE blends show two melting temperatures, which indicate that the blends were immiscible, and it was found that the melting temperature decreased for PP and increased for HDPE as the amount of HDPE increased in the blend. As the

ZnO nanoparticles were added to the blends, it was found that the melting temperatures improved for both polymers, which indicates that the ZnO addition worked as a filler between the polymeric chains, which restricted the motion and thus improved the Tm. In addition, it was found that the crystallization temperature improved slightly for 90/10 blends as the amount of ZnO increased and decreased for 80/20 blends. This is due to the higher amount of HDPE, which prevents the formation of large crystals even in the presence of ZnO particles. In addition, it is found that the degree of crystallinity χc was improved for both blends 90/10 and 80/20 as the amount of ZnO increased, except for 90/10/3% of ZnO, which decreased, which could be attributed to the distribution of ZnO during the sample preparation. From the above results, it is found that these results are in good agreement with the results of mechanical properties. The overall data that was observed from this test is shown in Table 4. These results are in agreement with [23], [24].
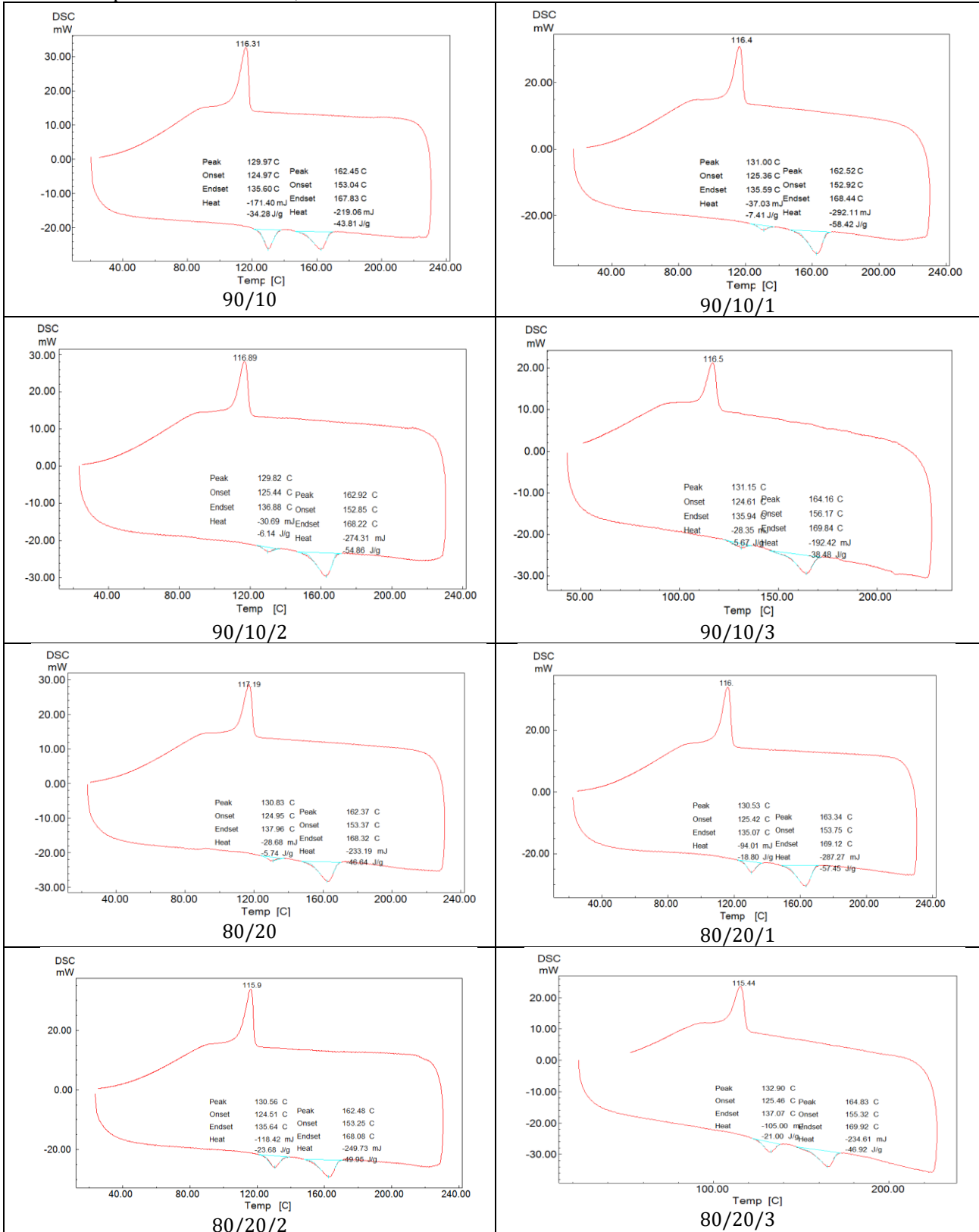

Figure 8: DSC curves for PP/HDPE blends and its composites with ZnO nanoparticles.

Table 4: DSC data for PP/HDPE, and its composites with ZnO nanoparticles.

PP/HDPE (wt.%)	ZnO (wt.%)	T_m (C°)		ΔH_m (J/g)		T_c (C°)	χ_c
		$T_{m(PP)}$	$T_{m(PE)}$	$\Delta H_{m(PP)}$	$\Delta H_{m(PE)}$		
90/10	-	162.45	129.97	43.81	34.28	116.31	18.87
90/10	1	162.52	131.0	58.42	7.41	116.4	25.16
90/10	2	162.92	129.82	54.86	6.14	116.89	23.62
90/10	3	164.16	131.15	38.48	5.67	116.5	16.60
80/20	-	162.37	130.83	46.64	5.74	117.19	17.85
80/20	1	163.34	130.53	57.45	18.8	116	22
80/20	2	162.48	130.56	49.95	23.68	115.9	19.11
80/20	3	164.83	132.9	46.92	21.0	115.44	17.96

3.4. FTIR analysis

FTIR spectroscopy was used to characterize the effect of ZnO addition on the chemical structure of PP/HDPE blends. Figure 9 shows the FTIR spectrum for PP/HDPE and PP/HDPE/ZnO in the range of 400–4000 cm^{-1}. Table 5 lists the most important band for the polymeric blends and their nanocomposite, as derived from figure 9 and compared with the band in [25]–[27]. For the PP/HDPE blend, the following bands were identified: the peaks that appeared at 2924.08 cm^{-1} and 2846.93 cm^{-1} are related to the CH_2 asymmetric and CH_3 symmetric stretch vibrations. The peaks at 1458.18 cm^{-1} and 1381.03 cm^{-1} are related to CH_3 symmetric bending. The peak at 1157.29 cm^{-1} is related to CH wagging, while the peaks at 810.10 cm^{-1} and 717.52 cm^{-1} are related to C-C stretch and CH_2 rocking. For the PP/HDPE/ZnO blend nanocomposite, the same bands appeared with a slight shift in peak band values. However, the band values at 485 cm^{-1} and 625 cm^{-1} are due to the stretching vibration of Zn-O [28]. Based on these results, it is clear that only physical interaction occurs between the blend of PP/HDPE and ZnO nanoparticles (not chemical interaction). No new bands appear or disappear within the IR spectrum; there is no chemical reaction, only physical interaction.
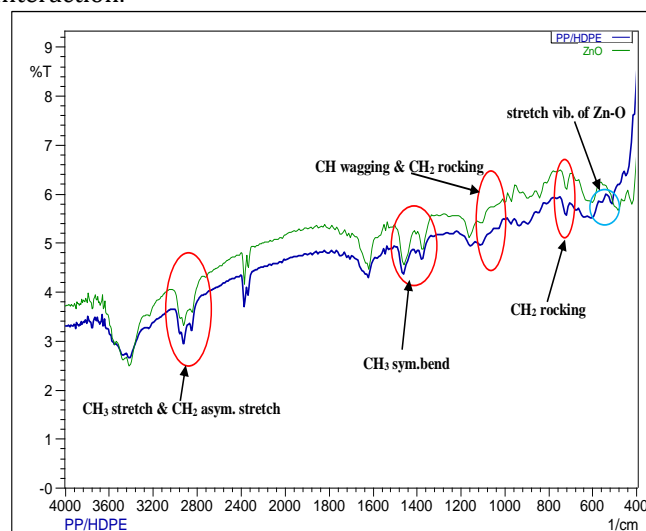

Figure 9: FTIR spectrums for PP/HDPE blends and its composites with ZnO nanoparticles.

Table 5: IR band Values for PP/HDPE and its composites with ZnO nanoparticles.

Bond type	PP	HDPE	PP/HDPE	PP/HDPE/ZnO
CH_2 rocking	-	720	717	717
C-C stretch	808	-	810	802
CH wagging CH_2 rocking	1166	-	1157	1165
CH_3 sy.bend	1376	-	1381	1373
	1456	1464	1458	1458
CH_3 stretch	2870	2850	2846	2846
CH_2 asy.stretch	-	2919	2924	2924
CH_3 asy.stretch	2950	-	-	-

4. CONCLUSIONS

From the above results, it can be concluded that the PP/HDPE blends are immiscible and have low mechanical and thermal properties. In addition, 90/10 and 80/20 blends have the highest mechanical and thermal properties. However, the addition of ZnO nanoparticles to the 90/10 and 80/20 blends by 1%, 2%, and 3% wt. had a good effect on the mechanical and thermal properties. The mechanical properties (tensile properties and Shor D hardness) were improved due to the higher properties of ZnO nanoparticles and also due to the stiffening effect that was caused by ZnO addition, and it was found that the highest tensile strength was at 2% wt. of ZnO and the highest Shor D hardness were found for 90/10 at 1% wt. of ZnO and for 80/20 at 2% wt. of ZnO. Also, the thermal properties, such as the melting temperature Tm and crystallization temperature Tc, were improved for both 90/10 and 80/20 blends, and the degree of crystallinity χ_c was increased for 90/10 and decreased for 80/20. FTIR analysis shows that there is no chemical interaction between PP/HDPE and ZnO nanoparticles.

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