

PROPERTIES OF POLYMER COMPOSITES FILLED WITH SiO₂, ZnO AND Mg(OH)₂ NANO POWDER¹

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Abstract

There are two typical ways to modify the properties of a raw polymer. One is polymer blending, which is a low-cost technique that gives rise to new materials with tailored properties. The other is the addition of mineral fillers and fibers, which has been extensively used to modify such properties of thermoplastics as rigidity, strength, durability, and hardness. In the case of immiscible blends, control of the morphology is fundamental; hence, the influence of such parameters as processing conditions and composition, mainly on compatibility, has been studied. In the case of filled polymers, the nature, shape, and size of the particles and their composition are critical parameters that will determine the properties of the composite. In this study, mechanical properties of the high density polyethylene (HDPE) composites filled with silicon dioxide (SiO₂), zinc oxide (ZnO) and magnesium hydroxide [Mg(OH)₂] were investigated. The structure and properties of the composites are characterized using a scanning electron microscopy (SEM) and Energy dispersive X-ray spectroscopy (EDS). Furthermore, HDPE composites were subjected to examinations to obtain their tensile strengths, yield strengths, elasticity modulus, % elongation, Izod impact strength, hardness, heat deflection temperature (HDT), Vicat softening point and melt flow index (MFI).

Key words: Silikon dioxide; Zinc oxide; Magnesium hydroxide; High density polyethylene.

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1 INTRODUCTION

Inexpensive inorganic substances are widely used as fillers to improve mechanical and thermal properties of polymers in the plastic industry. These mainly include fillers, such as calcium carbonate (CaCO_3), mica, wollastonite, glass fiber, glass beads, jute, silica (SiO_2) etc.⁽¹⁻³⁾

In recent years micro- and nano-fillers have attracted great interest, both in industry and in academia, because they often exhibit remarkable improvement in materials properties when compared to conventional composites made by using macro-fillers. These micro-/nano-composites can be made with very low loading of micro-/nano-fillers as compared with macro particle sized filler.⁽⁴⁾ High density polyethylene (HDPE) is widely used as a commodity polymer with high-tonnage production due to its distinctive mechanical and physical properties. Because of its low toughness, weather resistance, and environmental stress cracking resistance as compared to engineering polymers, its application in many areas has been limited. To improve these disadvantages, HDPE has been reinforced with fillers.⁽⁵⁻⁷⁾

Polyolefin composites based on silica have aroused great interest among researchers. Silica can be more effective in improving the mechanical strength and abrasion resistance of polypropylene (PP) and high density polyethylene (HDPE) than do ordinary fillers because of its small size and the surface-interface effect.⁽⁸⁻¹⁵⁾

ZnO as functional inorganic filler has been widely used in functional devices, catalysts, pigments, optical materials, cosmetics, and ultraviolet (UV) absorbers.^(16,17)

In addition, after Sawai and coworkers^(18,19) found that ZnO powder had antibacterial activity against some bacteria strains in 1995; more and more researchers have embarked on studies of ZnO as an antibacterial agent. Therefore, the introduction of ZnO into polymers can not only enhance the mechanical properties of the polymers because of a strong interfacial interaction between polymers and nanoparticles but also endow polymers with some other functional capabilities, such as photo stabilization^(20,21) and antibacterial activity.⁽²²⁾ Work has been reported on many aspects of $\text{Mg}(\text{OH})_2$ filled polymer composites, including its flame retardancy, mechanical properties, preparation and processing, crystallization and morphology, thermal oxidative degradation, rheology, interface and microstructure, and functional modification, but there are a few reports on the effects of particle size. Zhang et al. reported that effect of particle size on the properties of $\text{Mg}(\text{OH})_2$ filled rubber composites.⁽²³⁾ Mishra et al. investigated the effect of nano- $\text{Mg}(\text{OH})_2$ on the mechanical and flame retarding properties of PP composites.⁽²⁴⁾ In this article, 5 wt%, 10 wt%, 15 wt% and 20 wt% of SiO_2 , ZnO and $\text{Mg}(\text{OH})_2$ powder, as fillers and HDPE as polymer matrix, were used to prepare the polymer composites. The effect of all particles on the mechanical, thermal and morphological properties of HDPE was investigated.

2 EXPERIMENTALS AND METHODS

Thirteen different polymer composites (Table 1) were prepared by using the following materials: HDPE, known as Petilen YY (I 668 UV), was obtained from Petkim, Petrokimya Holding A.S., Turkey. Silicon dioxide (SiO_2), known as CAB-O-SIL TS-610, was obtained from CABOT, Billerica, MA-USA. Its specific gravity is 2.2 g/cm^3 and average particle length is 0.2 micron to 0.3 micron. Zinc oxide powder (MKN-ZnO-050) was supplied by MKnano (Ontario-Canada). Particle size (TEM) is $\leq 50 \text{ nm}$ and its purity is 99.9%. Magnesium hydroxide powder (MKN- $\text{Mg}(\text{OH})_2$ -050)

was supplied by MKnano (Ontario - Canada). Its purity is 99%. Particle size is 50 nm. SiO₂, ZnO and Mg(OH)₂ were dried in a Vacucell VD 55 vacuum oven (MMM - Medcenter Einrichtungen GmbH, München, Germany) at 105°C for 24 hours before being blended with HDPE. Mechanical premixing of solid compositions was done using a LB-5601 liquid-solids blender (The Patterson-Kelley Co., Inc. east Stroudsburg, PA, USA) brand batch blender for 15 min. Samples with various proportions of HDPE/SiO₂, HDPE/ZnO and HDPE/Mg(OH)₂ polymer composites were produced between 180°C-220°C at 20 bar to 30 bar pressure, and a rotation rate of 30 rpm, with a Microsan co-rotating twin-screw extruder (Microsan Instrument Inc. Kocaeli, Turkey). L/D ratio is 30, Ø: 25 mm. To prepare the samples for thermal and mechanical tests, the following injection conditions were used: Injection temperature was 180°C-220°C, injection pressure was 110 bar-130 bar, dwelling time in mold was 10 s, and screw rotation was 25 rpm, Polymer composites were also dried in vacuum oven at 105°C for 4 hours after extrusion.

Table 1. Composition of the different polymer composite formulations

Groups	HDPE (wt %)	SiO ₂ (wt %)	ZnO (wt %)	Mg(OH) ₂ (wt %)
1	100	-	-	-
2	95	5	-	-
3	90	10	-	-
4	85	15	-	-
5	80	20	-	-
6	95	-	5	-
7	90	-	10	-
8	85	-	15	-
9	80	-	20	-
10	95	-	-	5
11	90	-	-	10
12	85	-	-	15
13	80	-	-	20

Composite specimens were conditioned at 23°C and 50% humidity for 24 h before testing (ASTM D618). Tensile tests were prepared according to the ASTM D638 standards by using a Zwick Z010 (Ulm-Germany) testing machine with a load cell capacity of 10 kN at a cross-head speed of 50 mm/min. The hardness test was done according to the ASTM D2240 method with Zwick hardness measurement equipment. To investigate fracture behavior, Izod impact test (notched) was done at room temperature according to the ASTM D256 method with Zwick B5113 impact test device (Ulm, Germany). The fractured surfaces of the composites were coated to an approximate thickness of 10 nm of a gold (Au) (80%)/ palladium (Pd) (20%) alloys to prevent electrical charging by Polaron SC 7620 (Bad Schwalbach-Germany). The surfaces of the prepared samples were observed by the JEOL-JSM 5910 LV (Tokyo, Japan) scanning electron microscopy (SEM) at an acceleration voltage of 20 kV. Elemental analysis was done using Energy dispersive X-ray spectroscopy (EDS) (Oxford Instruments, England). Seven samples were tested in each set and the average value was reported.

3 RESULTS AND DISCUSSION

Mechanical properties of the HDPE/SiO₂-ZnO-Mg(OH)₂ polymer composites are given in Figure 1.

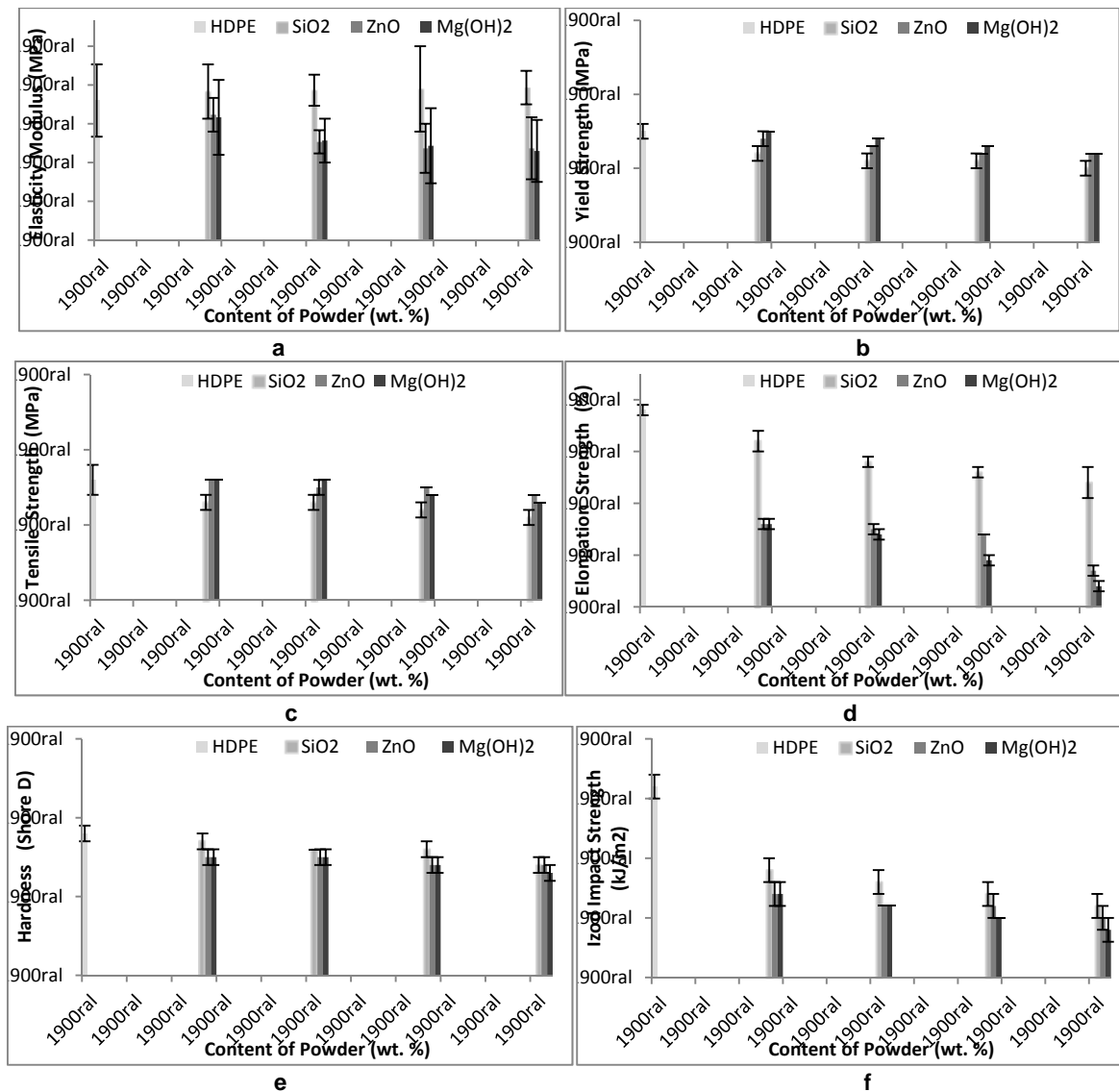


Figure 1. Mechanical properties of the HDPE polymer composites.

Elasticity modulus is the stiffness (the ratio between stress and strain) of a material at the elastic stage of a tensile. The effects of particle loading on the elastic modulus of HDPE/ SiO₂-ZnO-Mg(OH)₂ composites are given in Figure 1a. The elasticity modulus of HDPE/SiO₂ composites increased as the filler concentration increases from 5 wt% to 20 wt%. But, the elasticity modulus of HDPE/ZnO and HDPE/Mg(OH)₂ composites decreased as the filler concentration increases from 0 wt% to 20 wt%. This was due to agglomeration of particles at higher percentage and weak adhesion between fillers and the HDPE matrix. The minimum elasticity modulus is observed at the 20 wt% Mg(OH)₂ concentration for HDPE. The effect of particle loading on the yield strength and tensile strength of high density polyethylene/SiO₂-ZnO-Mg(OH)₂ composites are shown in Figure 1b and Figure 1c respectively. There is no significant change about the values. The elongation at break of SiO₂-ZnO-Mg(OH)₂ filled composites was measured (Figure 1d). With increased loading, the elongation at break of all

composites filled with $\text{SiO}_2\text{-ZnO-Mg(OH)}_2$ are decreased for all. The minimum elongation at break is observed at the 20 wt% Mg(OH)_2 concentration for HDPE. In comparison with the elongation at break of virgin HDPE, the elongation at break decreased by 79% for the composites with a 20 wt% Mg(OH)_2 concentration. The relationship between the filler content and the hardness of the polymer composites is shown in Figure 1e. There is no significant change about the values. Figure 1f illustrates the effect of filler on the Izod impact strength (notched) of HDPE composites. The impact strength decreased as the particle concentration increased from 0 wt% to 20 wt%. Fracture propagation was more pronounced with the addition of the particles. It is possible that all type of fillers agglomerated easily into large particles, which could be sites for crack propagation, and acted as a micro-crack initiator. In comparison with the Izod impact strength of virgin HDPE, the Izod impact strength decreased by 75% for the composites with a 20 wt% Mg(OH)_2 concentration. To sum up the above, it is clear that particle loading has an important effect on the composite toughness, which can be improved or reduced with changing particle loading.

Thermal properties of the HDPE/ $\text{SiO}_2\text{- ZnO-Mg (OH)}_2$ polymer composites are given in Figure 2. The relationship between the wt% of the filler and melt flow index of HDPE composites is shown in Figure 2a. Melt flow index of HDPE composites shows a decreased as the all fillers concentration increases from 0 wt% to 20 wt%. In comparison with the melt flow index of virgin HDPE, the melt flow index decreased by 52% for the composites with a 20 wt% Mg(OH)_2 filler concentration. As a result, higher filler content showed lower MFI value. The HDT and Vicat softening temperatures of composites samples are summarized in Figures 2b and 2c respectively. The HDT and Vicat experiment were started at room temperature with a heating rate of 120°C/h and under a load of 1.8 MPa and 1 Kg respectively. With the addition of SiO_2 , ZnO and Mg (OH)₂ in HDPE polymer has been a change in values. HDT values increased while Vicat values decreased. The Vicat temperature of virgin HDPE and HDPE/ SiO_2 (20 wt%) polymer composites were 134°C and 129°C respectively. The HDT values of the HDPE/ $\text{SiO}_2\text{- ZnO-Mg(OH)}_2$ increased with an increase weight percentage of fillers from 0 wt% to 20wt%. The maximum HDT is observed at the 20 wt% ZnO concentration for HDPE composites.

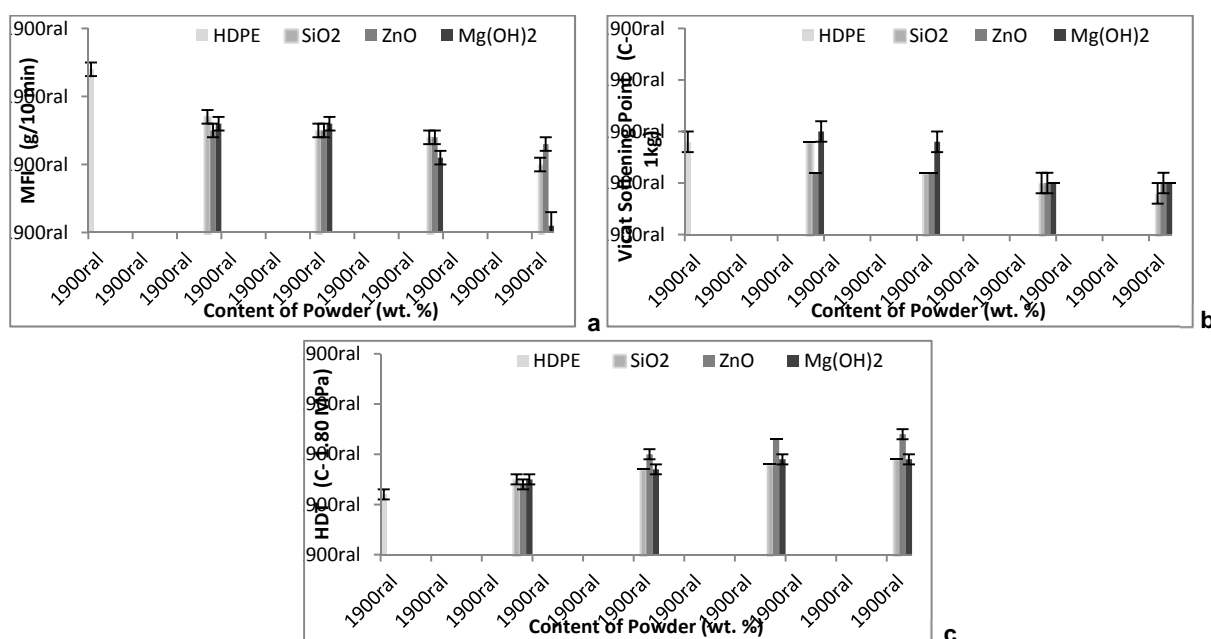


Figure 2. Thermal properties of the HDPE polymer composites.

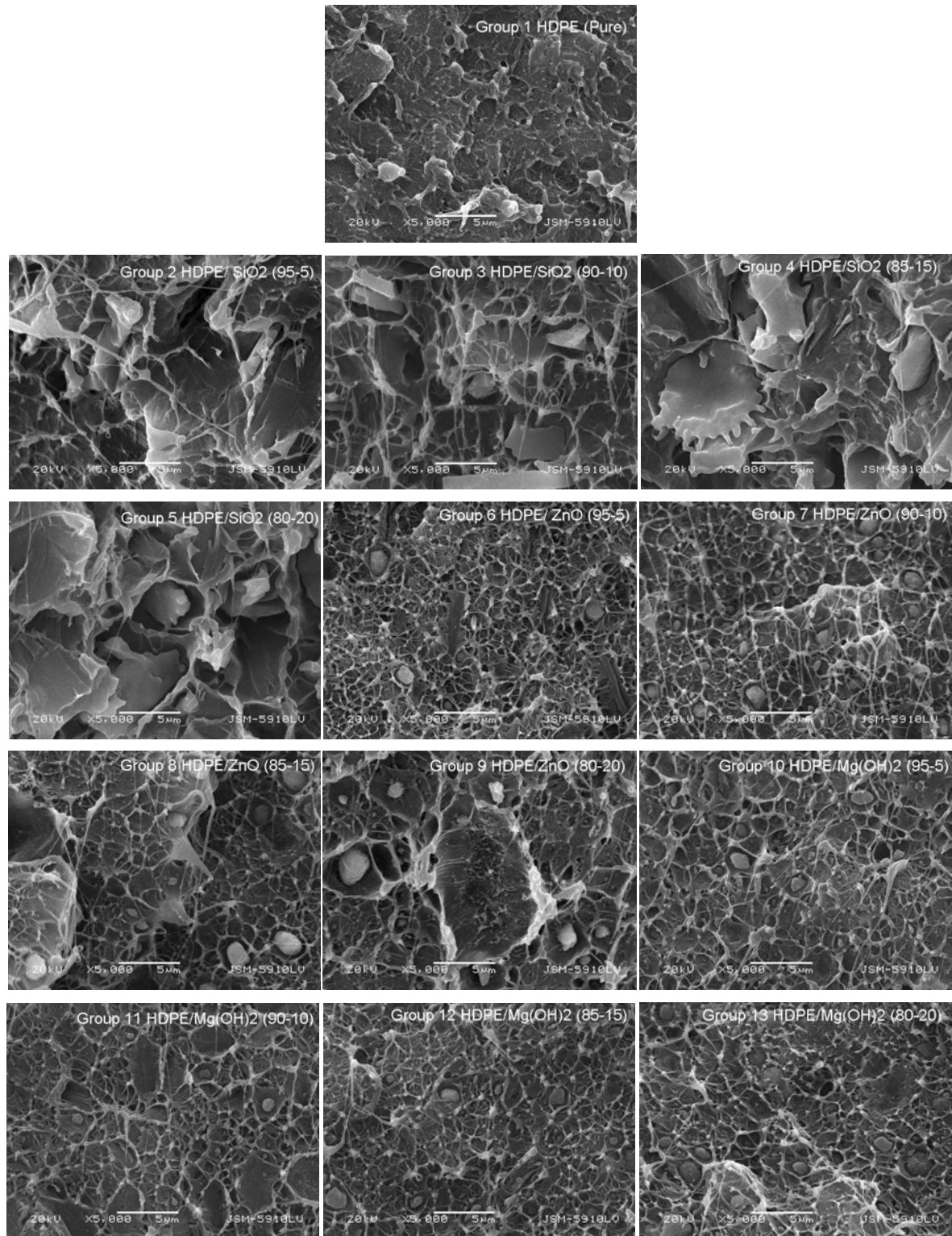


Figure 3. SEM micrographs of the HDPE polymer composites.

The micrographs taken from the fracture surface of HDPE, HDPE/SiO₂, HDPE/ ZnO and HDPE/Mg(OH)₂ composite samples are shown in Figure 3 and energy dispersive X-ray spectroscopy spectrums of the polymer composite are shown in Figure 4. The boundaries and the contrast can be obviously seen between the two phases of SiO₂, ZnO and Mg(OH)₂ particles and HDPE matrix. The micrographs indicate that the particulates are homogeneously dispersed on the fractured surfaces of polymer matrix. But the bond between the polymer and particles is weak. Large particles

indicate that some of the particles coalesced into a single particle during processing of the composite. As seen from the figure, addition of particles resulted in porous structure. This can be seen clearly from Figure 3.

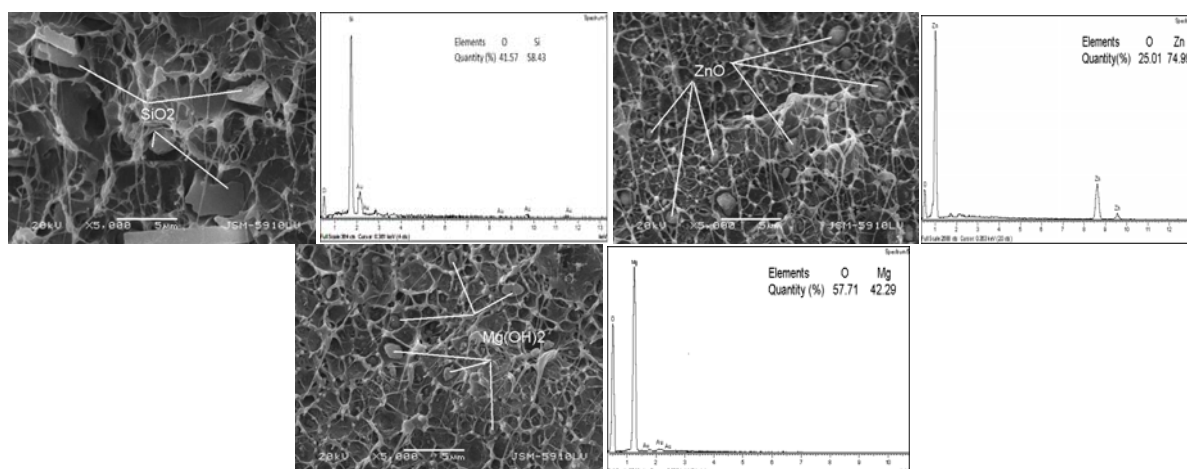


Figure 4. Energy dispersive X-ray spectroscopy (EDS) spectra of the HDPE polymer composite.

4 CONCLUSIONS

In the present work, mechanical, thermal and morphological properties of SiO₂, ZnO and Mg (OH)₂ filled HDPE polymer composites were investigated. It was found that introduction of SiO₂, ZnO and Mg (OH)₂ particles into HDPE reduced the elasticity modulus (except SiO₂), % elongation, hardness and Izod impact strength (notched) of HDPE. Rate of decrease in Izod impact strength and % elongation was large, when 5 wt% SiO₂, ZnO and Mg (OH)₂ were first added into HDPE. Increasing the wt% of particles from 5 wt% to 20 wt%, a slower decrease in Izod impact strength and % elongation was observed. As compared with the Izod impact strength and % elongation of unfilled HDPE, Izod impact strength and % elongation of 20 wt% Mg(OH)₂ filled HDPE were lower, about 75% and 79% respectively. On the other hand, there was no significant change about the yield strength and tensile strength values. Also, the results showed that MFI and Vicat values of composites decreased with increasing particle loading but HDT values increased with increasing particle loading. The micrographs indicate that the SiO₂, ZnO and Mg(OH)₂ particulates are homogeneously dispersed on the fractured surfaces of polymer matrix. But the bond between the polymer and particles is weak and, addition of particles resulted in porous structure. The SEM micrograph also shows the agglomeration of SiO₂, ZnO and Mg(OH)₂ particles. It is known that this type of particles have a great tendency to form agglomerates, in fact, agglomeration is a well-known phenomenon, and its probability increases with decreasing particle size. As shown by the mechanical properties (Figure 1), the reduction of the impact resistance properties in direct proportion to the increase in the amount of fillers was thought to be the reason for the aforementioned defaults.

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