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Zinc oxide (ZnO), magnesium hydroxide [$Mg(OH)_2$] and calcium carbonate ($CaCO_3$) filled HDPE polymer composites: Mechanical, thermal and morphological properties

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Abstract

Polymer nanocomposites represent a new alternative to conventionally filled polymers. Because of their nanometer sizes, filler dispersion nanocomposites exhibit markedly improved properties when compared to the pure polymers or their traditional composites. These include increased modulus and strength, outstanding barrier properties, improved solvent and heat resistance and decreased flammability. In this study, mechanical, thermal and morphological properties of the high density polyethylene (HDPE) composites filled with nano zinc oxide ZnO), magnesium hydroxide [$Mg(OH)_2$] and calcium carbonate ($CaCO_3$) 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, wear strengths, heat deflection temperature (HDT),Vicat softening point and melt flow index (MFI).

Key words: Magnesium hydroxide, calcium carbonate, zinc oxide, high density polyethylene, polymer composites

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INTRODUCTION

High-density polyethylene (HDPE) is one of the most common materials because of its excellent flexibility, good process ability, and low cost. However, its use is restricted because of its lower strength, photo degradation, poor compatibility with polar inorganic fillers leads to a decrease in the mechanical properties of the composites and so on [1-4].

In recent years, thermoplastic resin/mineral filler composites have been widely used in molded products due to effective cost reduction. Generally, the addition of mineral fillers will have an embrittling effect on polymers although the rigidity of the polymers can be increased [5-7]. Much effort has been devoted to improving the properties of polymers by the addition of inorganic fillers, such as SiO_2,[8] ZnO,[9-10], $CaCO_3$,[11] and carbon fibers [12].

Calcium carbonate is the second most widely used mineral filler after talc. The use of $CaCO_3$ with a suitable hardness (Mohr hardness ~3) does not cause short-term failure in processing machinery [13]. The adhesion between the filler and the matrix is very important for polymer composites. If the adhesion is strong in the interface, the modulus, rigidity, strength, and toughness of a particulate composite will be increased. Many mineral fillers and $CaCO_3$ are based on inorganic materials that do not exhibit good adhesion to thermoplastic matrices. Therefore, the surface modification of filler particles with suitable coupling agents is often recommended to enhance filler particle dispersion into polymer matrices to improve strong bonding with the matrix and molding [14]. HDPE filled with mineral particles also improves dimensional stability, opacity, and barrier properties. $CaCO_3$ is the largest volume mineral used in the polymer industry because of its low cost and abundance. It is available globally in a variety of particle shapes, purities, and sizes (micro and nano). However, because of its higher polar nature and higher surface areas, $CaCO_3$ is difficult to disperse and stabilize in a polymer matrix [15-18]. The effect of addition of nanosized calcium carbonate with polyethylene on tensile properties, viscosity, and dimensional stability has been investigated by some researchers. Lazzeria et al.[19] fabricated PE nanocomposite with 70% improved Young’s modulus compared to virgin PE. The creep behavior of PE nanocomposites reinforced with different nanosized calcium carbonate depends strongly on the calcium carbonate content. One study showed that the best creep resistance of PE nanocomposites can be achieved at 10% of calcium carbonate incorporation in the composite [20]. Zebarjad et al. reported that nanosized calcium carbonate has a significant effect on crystallinity, melting point, and heat of melting of HDPE. Additionally, calcium carbonate could have a significant effect on rheological behavior of HDPE. Moreover, decreasing CaCO3 particle size from micro to nano could affect the barrier properties of the composite [21].

ZnO as functional inorganic filler has been widely used in functional devices, catalysts, pigments, optical materials, cosmetics, and ultraviolet (UV) absorbers [22, 23]. In addition, after Sawai and coworkers [24, 25] 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 photostabilization [26,27] and antibacterial activity [3,28].

In the last few decades, work has been reported on many aspects of $Mg(OH)_2$ 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 $Mg(OH)_2$ filled rubber composites [29]. Mishra et al. investigated the effect of nano- $Mg(OH)_2$ on the mechanical and flame retarding properties of PP composites [30]. Patil et al. investigated the

effect of nano-magnesium hydroxide on mechanical and flame retarding properties of styrene butadiene rubber and polybutadiene rubber [31]. Sheng et al. reported that dispersion, thermal and mechanical properties of polypropylene/magnesium hydroxide nanocomposites compatibilized by SEBS-g-MA [32].
In this study, the effects of the ZnO, $Mg(OH)_2$ and $CaCO_3$ concentration on the mechanical, thermal and morphological properties of HDPE composites were investigated. To this end, HDPE polymer composites containing 5, 10, 15 and 20 wt % ZnO, $Mg(OH)_2$ and $CaCO_3$ were produced, and the properties of the composites were investigated.

EXPERIMENTAL

Compositions and Materials:

Thirteen different polymer composites were prepared. Compositions of HDPE/ZnO, HDPE/ $Mg(OH)_2$ and HDPE/$CaCO_3$ polymer composites that were formed are given in Table 1.

Table 1 Composition of the different polymer composite formulations

Groups	HDPE (wt %)	ZnO (wt %)	$Mg(OH)_2$ (wt %)	$CaCO_3$ (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

High-density polyethylene (HDPE) (I 668 UV) was supplied by Petkim (Izmir-Turkey). Specific gravity is 0,970 g/cm^3. Melt flow rate is 5.2 g/10 min (190^oC–2.16 Kg). Yield strength is 28,0 MPa and notched Izod impact (23^oC) is 12 kJ/m^2. Zinc oxide nano powder (MKN-ZnO-050) was supplied by MKnano (Ontario-Canada). Particle size (TEM) is $\leq$50 nm and white powder. Its purity is 99.9 %. Magnesium hydroxide nano powder (MKN-$MgOH_2$–050) was supplied by MKnano (Ontario - Canada). Its purity is 99 %. Particle size is 50 nm. Calcium carbonate (calcite- $CaCO_3$) nanopowder (Calprec PR) was supplied by Cales de Llierca (Girona-Spain). Its purity is 98 %. Particle diameter is 50 nm.

Composite Preparation:

ZnO, $Mg(OH)_2$ and $CaCO_3$ was dried in a Vacucell VD 55 vacuum oven **(**MMM Medcenter Einrichtungen GmbH**,** München- Germany) at 105 ^oC 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/ZnO, HDPE/$Mg(OH)_2$ and HDPE/$CaCO_3$ polymer composites were produced between 180-220 °C at 20-30 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, Ǿ: 25 mm, Polymer composites were also dried in vacuum oven at 105 °C for 4 hours after extrusion. Subsequently, test samples were molded in injection molding machine. Extrusion and injection conditions are given in Table 2.

Table 2 Extrusion and injection conditions of the HDPE polymer composites

Process	Extrusion	Injection
Temperature (° C)	180–220	180–220
Pressure (bar)	20-30	110–130
Waiting time in mold (s)	-	10
Screw speed (rpm)	30	25
Mould temperature (°C)	-	40

Test Procedure:

Composite specimens were conditioned at 23°C and 50% humidity for 24 h before testing (ASTM D618). Tensile tests were performed according to ASTM D638 specification. They were carried out using a Zwick Z010 (Zwick GmbH, Ulm-Germany) testing machine with a load cell capacity of 10 kN at a cross-head speed of 50 mm/min. The elastic modulus, yield strength, tensile strength and percent elongation was determined from the stress–strain curves. 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 (Zwick GmbH & Co. KG 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 (Gala Instrumente GmbH, Bad Schwalbach-Germany). The surfaces of the prepared samples were observed by the JEOL-JSM 5910 LV (JEOL Ltd.**,** Tokyo, Japan) scanning electron microscopy (SEM) at an acceleration voltage of 20 kV. Elemental analysis was done using Energy dispersive X-ray spectroscopy (EDS) (Incax-sight- model: 7274- Oxford Instruments, England). Seven samples were tested in each set and the average value was reported.

RESULTS AND DISCUSSION

Mechanical properties of the ZnO, $Mg(OH)_2$ and $CaCO_3$ filled HDPE

Mechanical properties of the HDPE/ZnO-$Mg(OH)_2$-$CaCO_3$ polymer composites are given in Table 3 and Figure 1

Table 3 Mechanical properties of the HDPE/ZnO-$Mg(OH)_2$-$CaCO_3$ polymer composites

Groups	Elasticity Modulus (MPa)	Yield Strength (MPa)	Tensile Strength (MPa)	Elongation @ Break (%)	Hardness (Shore D)	Izod Impact Strength (kJ/m^2) (notc.)
1	138±28	25±1	26±1	43±1	58±1	16±1
2	127±13	24±1	26±0	21±1	55±1	7±1
3	106±9	23±0	25±1	20±1	55±1	6±0
4	101±19	22±0	25±0	19±0	54±1	6±1
5	101±24	22±0	24±0	12±1	54±1	5±1
6	125±29	25±0	26±0	21±1	55±1	7±1
7	107±17	24±0	26±0	19±1	55±1	6±0
8	103±29	23±0	24±0	14±1	54±1	5±0
9	99±24	22±0	23±0	9±1	53±1	4±1
10	117±25	24±0	26±0	18±2	56±0	6±0
11	113±11	23±0	25±0	16±3	56±1	6±1
12	100±10	23±0	24±0	14±1	55±1	6±1
13	95±11	23±0	24±0	11±1	55±0	6±1

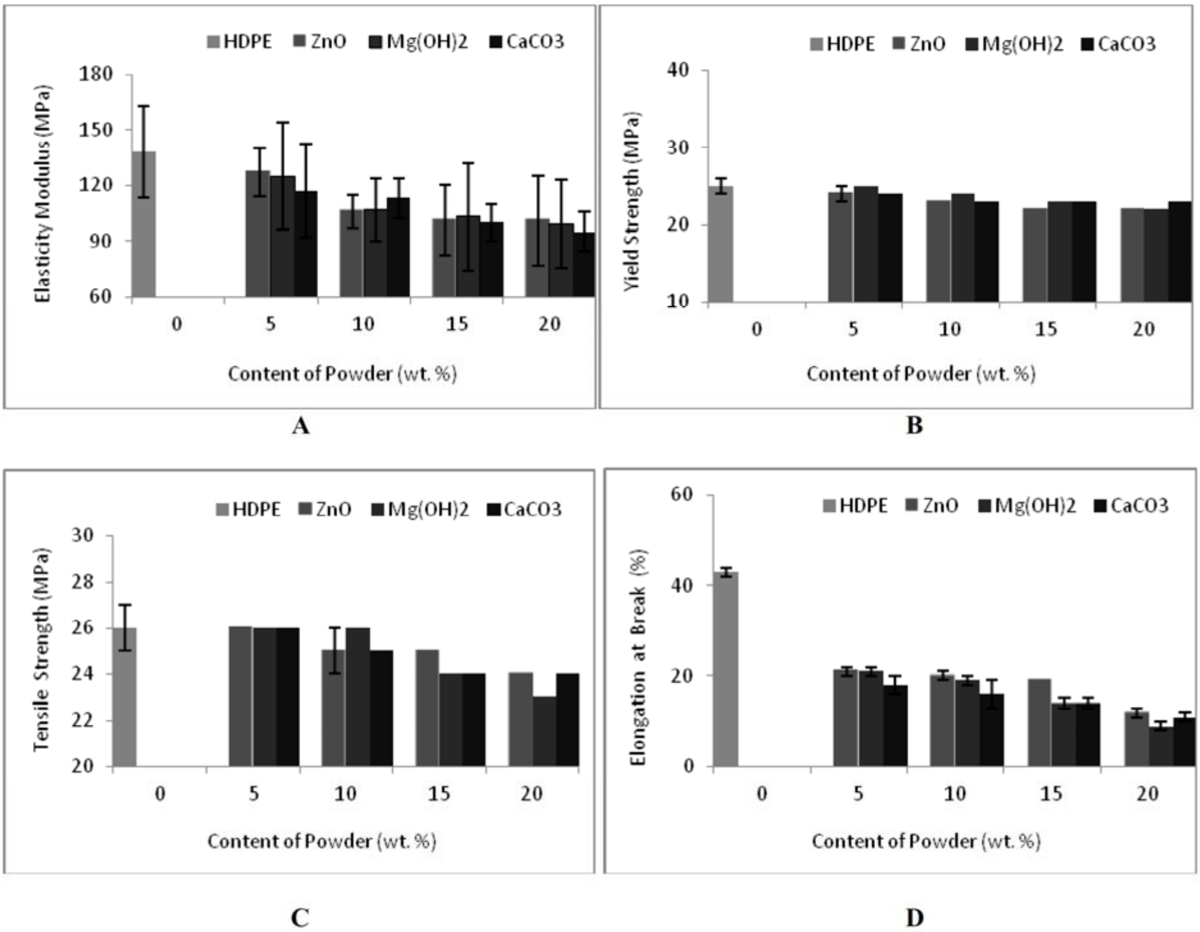
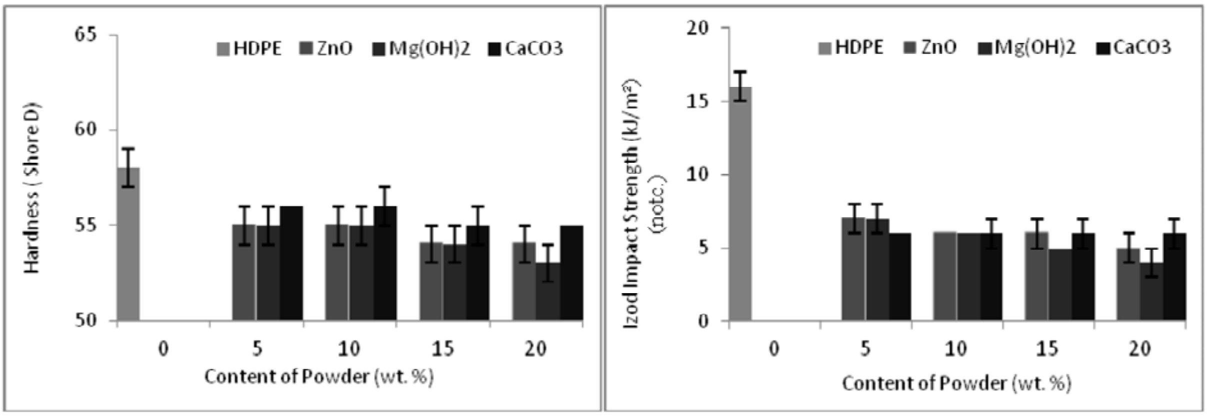


Figure 1 Mechanical properties of the HDPE polymer composites



E **F**

Figure 1 (continue)

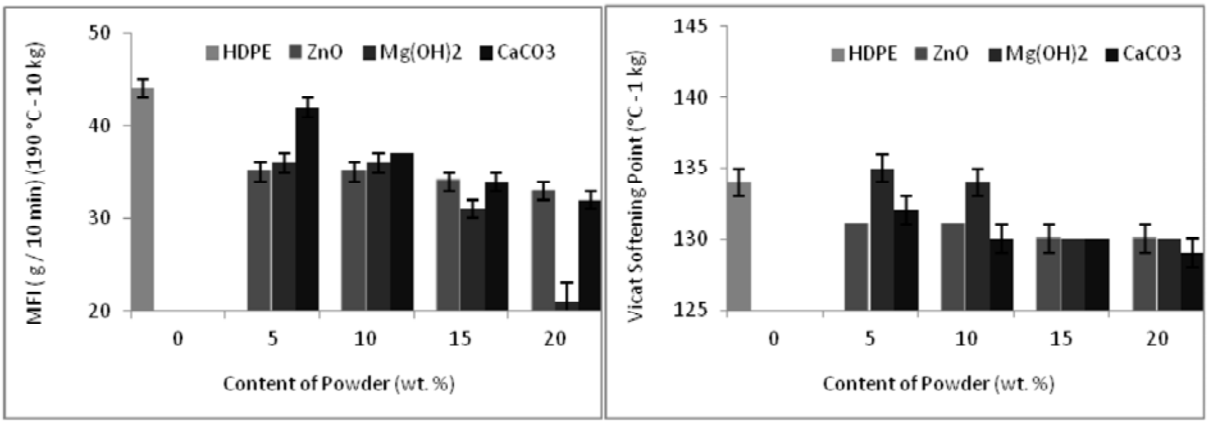
Elasticity modulus is the stiffness (the ratio between stress and strain) of a material at the elastic stage of a tensile. The effects of particle loading on the elastic modulus of HDPE/ ZnO-Mg $(OH)_2$-$CaCO_3$ composites are given in Figure 1-A. It is seen that the modulus is affected by particle size in the range studied. The elasticity modulus of HDPE/ZnO-Mg $(OH)_2$-$CaCO_3$ composites decreased as the filler concentration increases from 0 to 20 wt %. Above 5 wt %, a decrease in elasticity modulus is observed coinciding with the agglomeration of particles at higher percentage of fillers. Also this was due to weak adhesion between fillers and the HDPE matrix. The minimum elasticity modulus is observed at the 20 wt % $CaCO_3$concentration for HDPE. In comparison with the elasticity modulus of virgin HDPE, the elasticity modulus decreased by 31% for the composites with a 20 wt % $CaCO_3$concentration. The effect of particle size and loading on the tensile yield strength of high density polyethylene (HDPE)/ZnO-Mg $(OH)_2$-$CaCO_3$ composites is shown in Fig. 1-B. There is no significant change about the all values. The relationship between the ratio percentage of the fillers and ultimate tensile strength of HDPE composites is shown in the Figure 1-C. Ultimate tensile strength of composites showed no change as the fillers concentration in 5 wt %. But, ultimate tensile strength of HDPE composites shows a decrement as the filler concentration increases from 10 to 20 wt %. The minimum ultimate tensile strength is observed at the 20 wt % $Mg(OH)_2$ concentration for HDPE. In comparison with the elasticity modulus of virgin HDPE, the ultimate tensile strength decreased by 12% for the composites with a 20 wt % $Mg(OH)_2$ concentration. The elongation at break of ZnO, Mg $(OH)_2$ and $CaCO_3$ filled composites was measured, as shown in Figure 1-D. With increased loading, the elongation at break of all composites filled with ZnO, $Mg(OH)_2$ and $CaCO_3$ 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 1-E. The hardness of the composites decreased (from 0 to 20 wt %) with an increase weight percentage of fillers. The minimum hardness is observed at the 20 wt % $Mg(OH)_2$ concentration for HDPE (53 Shore D). In comparison with the hardness of virgin HDPE, the hardness decreased by 9 % for the composites at a 20 wt % filler concentration. Figure 1-F 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 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 ZnO, Mg $(OH)_2$ and $CaCO_3$ filled HDPE

Thermal properties of the HDPE/ ZnO-Mg $(OH)_2$-$CaCO_3$ polymer composites are given in Table 4 and Figure 2. The relationship between the wt % of the filler and melt flow index of HDPE composites is shown in the Table 4 and figure 2-A. Melt flow index of HDPE composites shows a decreased as the fillers concentration increases from 0 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 (group 9). On the other hand melt flow index of HDPE/$CaCO_3$ composites shows also a decrement as the filler concentration increases from 0 to 20 wt %. There is a not significant change in HDPE/ZnO polymer composites. As a result, higher filler content showed lower MFI value.

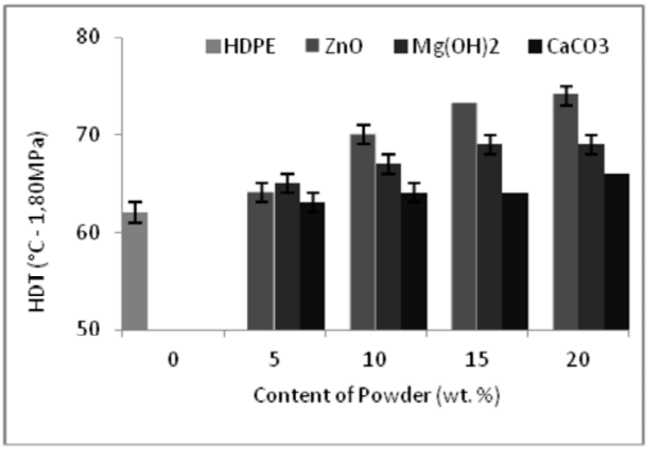
Table 4 Thermal properties of the HDPE/ZnO-$Mg(OH)_2$-$CaCO_3$ polymer composites

Groups	MFI (g/10min) (190 °C – 10 kg)	Vicat Softening Point (°C- 1 kg)	HDT (°C-1.80 MPa)
1	44±1	134±1	62±1
2	35±1	131±0	64±1
3	35±1	131±0	70±1
4	34±1	130±1	73±0
5	33±1	130±1	74±1
6	36±1	135±1	65±1
7	36±1	134±1	67±1
8	31±1	130±0	69±1
9	21±2	130±0	69±1
10	42±1	132±1	63±1
11	37±0	130±1	64±1
12	34±1	130±0	64±0
13	32±1	129±1	66±0



A **B**

Figure 2 Thermal properties of the HDPE polymer composites



C

Figure 2 (Continue)

The HDT and Vicat softening temperatures of composites samples are summarized in Table 4 and Fig 2-B and Fig 2-C 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 ZnO, Mg $(OH)_2$ and $CaCO_3$ in HDPE polymer has been a change in values. HDT values increased while Vicat values decreased. The Vicat temperature of virgin HDPE and HDPE/$CaCO_3$ (20 wt %) polymer composites were 134°C and 129°C respectively. The HDT values of the HDPE/ZnO increased with an increase weight percentage of ZnO from 0 to 20 wt%. Similar situation was seen in HDPE/$Mg(OH)_2$ and HDPE/$CaCO_3$ composites. The maximum HDT is observed at the 20 wt % ZnO concentration for HDPE composites. In comparison with the HDT of virgin HDPE, the HDT increased by 19% for the composites with a 20 wt % ZnO filler concentration. As a result, higher filler content showed lower Vicat values but higher HDT values.

Morphological properties of the ZnO, Mg $(OH)_2$ and $CaCO_3$ filled HDPE

The surface area is the major parameter in connection with filler-matrix interaction for reinforcing purposes. The filler dispersion and the phase morphology of neat HDPE filled with various content and type of particle were studied by SEM and shown in Figures 3, and energy dispersive X-ray spectroscopy (EDS) spectrums of the polymer composite are given in Figure 4. The scanning electron microscopy photographs (Fig.3) show the morphological characteristics of the impact fracture of HDPE/ZnO, HDPE/$Mg(OH)_2$ and HDPE/ $CaCO_3$ systems. The boundaries and the contrast can be obviously seen between the two phases of ZnO, Mg $(OH)_2$ and $CaCO_3$ particles and HDPE matrix. The micrographs indicate that the particulates are homogeneously dispersed on the fractured surfaces of polymer matrix. The fracture surface topologies of Izod impact test specimens were dependent on the filler content. As the filler size, shape, and loading directly affect the performance of composite. The SEM micrograph also shows the agglomeration of ZnO, Mg $(OH)_2$ and $CaCO_3$ 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. These agglomerated particles could be stress concentrator points and could affect the final performance of the composite. As shown by the mechanical properties (Fig 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.

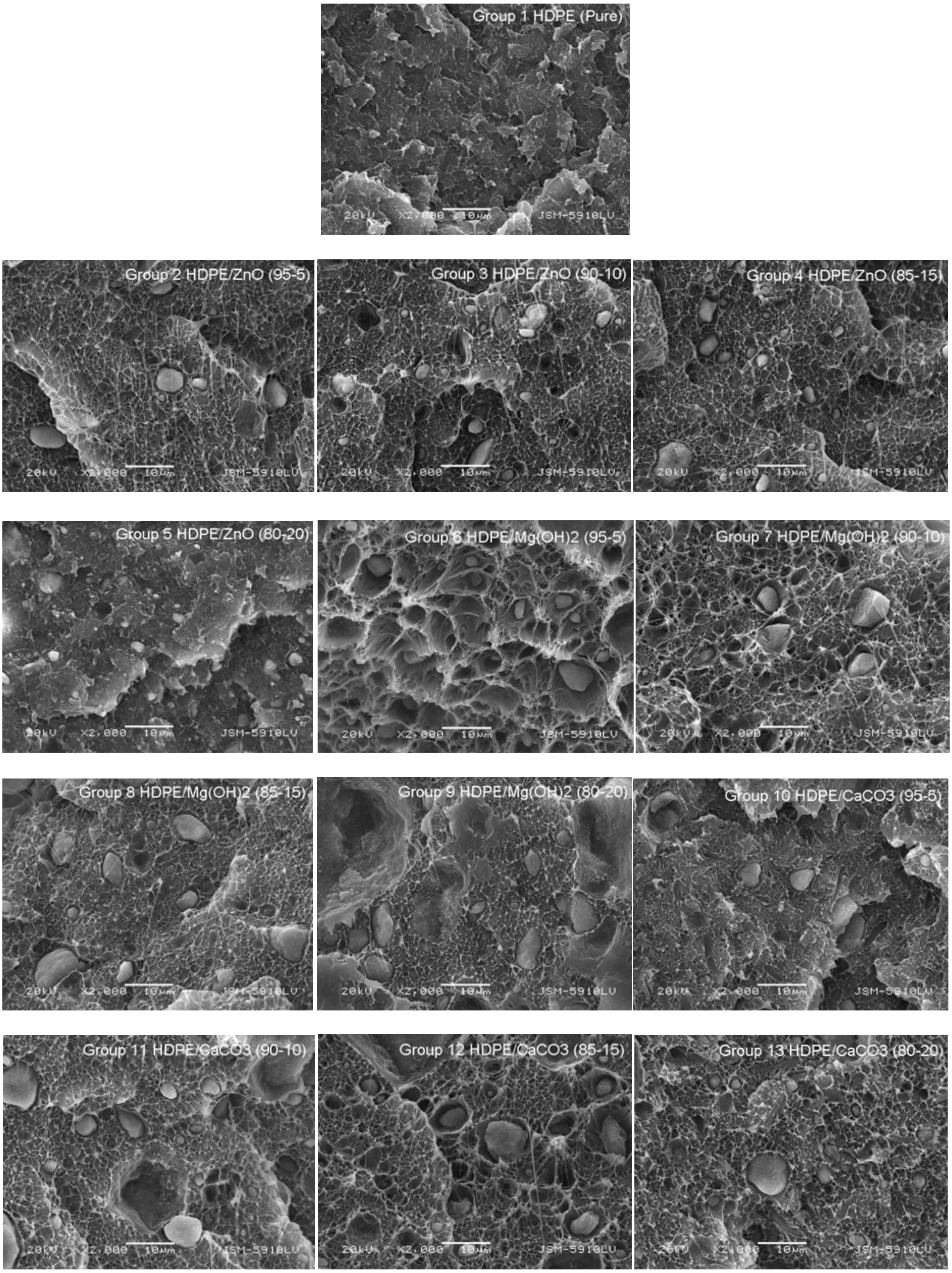


Figure 3 SEM micrographs of the HDPE polymer composites

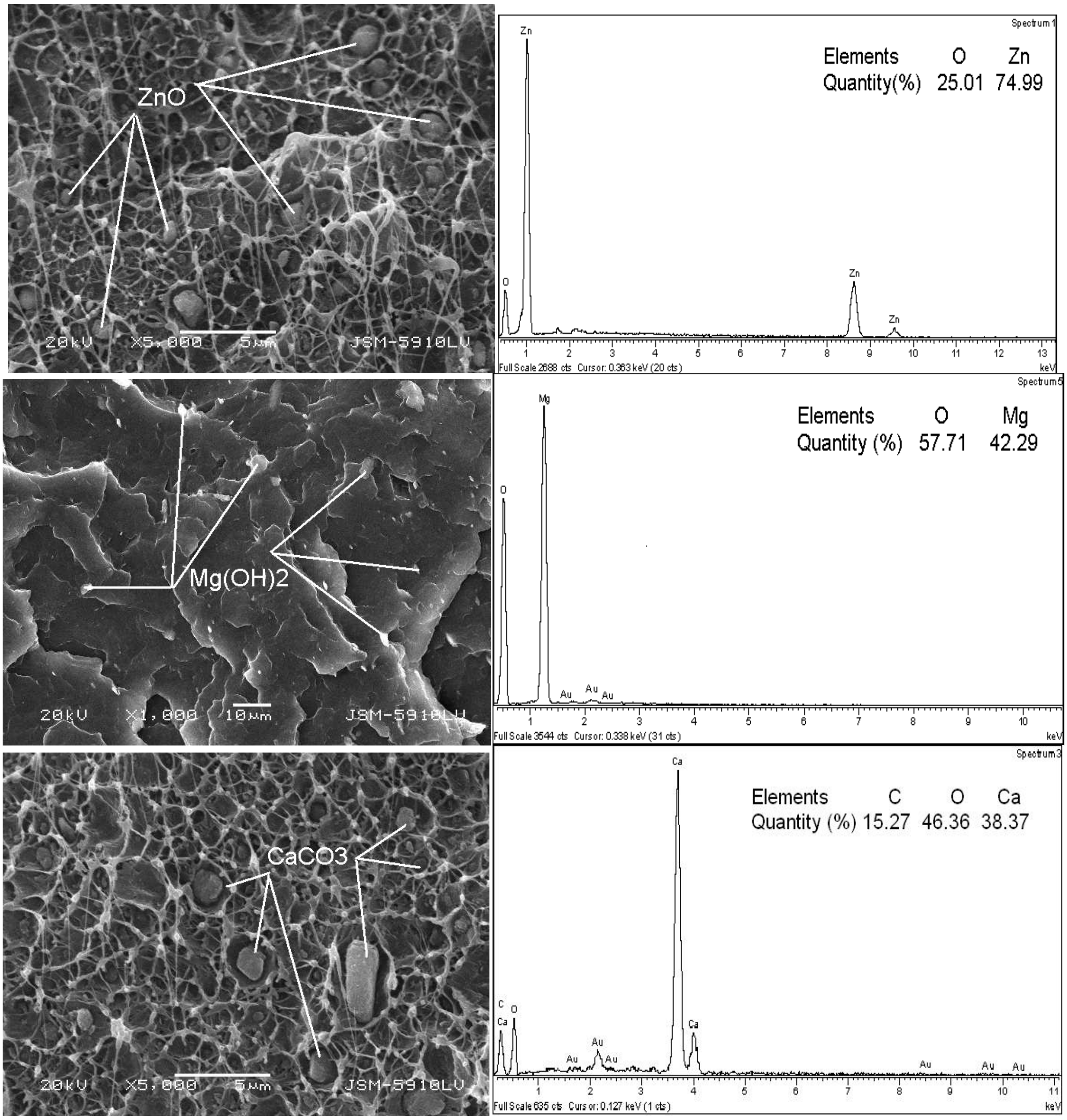


Figure 4 Energy dispersive X-ray spectroscopy (EDS) spectra of the HDPE polymer composite

CONCLUSIONS

HDPE polymer composites were successfully prepared by a simple compounding process. Experimental results of the mechanical, thermal and morphological properties of polymer based particulate ZnO, Mg $(OH)_2$ and $CaCO_3$ composites is presented. The results showed that the elasticity modulus, yield strength, tensile strength, % elongation, Izod impact strength and hardness of composites decreased with increasing particle loading. This was due to weak adhesion between fillers and the HDPE matrix and agglomeration of particles. 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 ZnO, Mg $(OH)_2$ and $CaCO_3$ particulates are homogeneously dispersed on the fractured surfaces of polymer matrix.

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