EFECTUL OXIDULUI DE ZINC ŞI AL BORATULUI DE ZINC ASUPRA PROPRIETĂȚILOR MECANICE ALE POLIETILENEI DE ÎNALTĂ DENSITATE

EFFECT OF ZINC OXIDE AND ZINC BORATE ON MECHANICAL PROPERTIES OF HIGH DENSITY POLYETHYLENE

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The effect of zinc oxide (ZnO) and zinc borate ($ZnHBO_3$) on the mechanical properties of high density polyethylene (HDPE) was investigated. Composites of HDPE with zinc oxide and zinc borate were prepared by melt mixing in a twin screw extruder and then the composites were molded by compression molding method. Filler contents in the HDPE were 5, 10 and 15 wt%.

The dispersion of zinc oxide and zinc borate particles in the matrix polymers was investigated using SEM. It was observed that the dispersion of ZnO and $ZnHBO_3$ particles were relatively good with low ZnO and $ZnHBO_3$ content but the aggregates of ZnO and $ZnHBO_3$ particles in a polymer matrix increased with increasing content. The mechanical test showed that the elasticity modulus, hardness and density of HDPE composites increased with increasing ZnO and $ZnHBO_3$ content. The addition of fillers to the HDPE changed the wear rate of the composites as well.

Keywords: *High density polyethylene, zinc oxide, zinc borate, mechanical properties, wear*

1. Introduction

Polymer nano composites have attracted increasing attention in recent years because of their significant improvement of physical and chemical properties over the matrix polymers. The effects of nanoparticles on these properties have been extensively investigated. The addition of just a few percent by weight of nanoparticles can result in significant improvement of mechanical properties. Many studies have been carried out focusing on the incorporation of rigid inorganic nanoparticles which is a promising approach to improve both stiffness and toughness of plastics simultaneously [1–5]. There is currently great interest in the introduction of inorganic particles to organic polymers because organic–inorganic composites offer an effective way to improve the physical properties of conventional polymers such as mechanical properties, thermal stability, flame retardancy, electrical properties, and chemical reagent resistant [6-11].

High density polyethylene 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. HDPE filled with mineral particles also improves dimensional stability, opacity, and barrier properties [12-15].

Zinc oxide (ZnO) particles are relatively easy to disperse, and compared to other particles such as aluminum oxide (Al_2O_3) or titanium dioxide (TiO_2), ZnO particles have almost no surface water [16]. ZnO as functional inorganic filler has been widely used in functional devices, catalysts, pigments, optical materials, cosmetics, and ultraviolet (UV) absorbers [17,18]. In addition, Sawai and coworkers [19,20] 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 [21,22] and antibacterial activity [23].

Zinc borate is used as a flame retardant and smoke suppressant for wide range of plastics, rubber, paper, and textiles. It can replace antimony oxide as synergist in plastics and rubber to enhance the activity of primary flame retardants by stepwise releasing the radicals in a wide variety of end – use products. It is also used in paints, adhesives, pigments and ceramic industries [24]. Zinc borate is the most consumed metal hydroxides

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for retarding polymer. One of the difficulties concerning metal hydroxides is the reduction of mechanical properties, especially strength property in samples which contain filler, is inferior compared to the samples which lacking any type of filler within them. This is probably due to lack of compatibility between polymer and filler which can be improved via various techniques [25].

In this study, composites of HDPE with zinc oxide and zinc borate were prepared by melt processing in a twin screw extruder and the effect of zinc oxide and zinc borate on the mechanical properties and morphology of composites was investigated. Analyses were carried out using universal tensile testing machine, pendulum impact tester, durometer hardness tester, HDT-Vicat testing machine and scanning electron microscope (SEM) to investigate the dispersion of ZnO&$ZnHBO_3$ its influence on the mechanical properties of composites.

2 Experimental

2.1 Compositions and materials

Seven different polymer composites were prepared. Compositions of HDPE/zinc oxide and zinc borate powder polymer composites that were formed are given in Table 1.

Table 1

Composition of the different polymer composites formulations

Groups	HDPE (wt %)	Zinc oxide (wt %)	Zinc borate (wt %)
1	100	-	-
2	95	5	-
3	90	10	-
4	85	15	-
5	95	-	5
6	90	-	10
7	85	-	15

HDPE, known as Petilen YY (I 668 UV), was obtained from Petkim, Petrokimya Holding A.S., Turkey. Its density is 0,970 g/cm^3, melt flow rate is 5.2 g/10 min at 190°C–2.16 kg, yield strength is 28.0 MPa and notched Izod impact is 50 J/m. Zinc oxide powder (MKN-ZnO-050) was supplied by MKnano (Ontario-Canada). Particle size (TEM) is ≤50 nm and its purity is 99.9 %. Zinc borate ($ZnHBO_3$) was obtained from Jinan ShiChao Chemical Co., Ltd., China.

Its particle diameter is ≤ 5.0 μ and specific gravity is 2.72 g/ml. Its concentration is B_2O_3 45.0-48.0% and ZnO 37.5-39.0%.

2.2. Sample preparation and mechanical characterization

HDPE, zinc oxide and zinc borate were dried in oven at 105 °C for 3 hours before melt extrusion. Mechanical premixing of solid compositions was done using a LB-5601 liquid-solids blender (The Patterson-Kelley Co., USA) brand batch blender for 15 min. Samples with various proportions of HDPE polymer composites were produced between 180-220 °C at 25-35 bar pressure and a rotation rate of 25 rpm with a Mikrosan extruder (Mikrosan Instrument Inc. Turkey). Polymer composites were also dried in oven at 105 °C for 3 hours after extrusion. Subsequently, test samples were molded in injection molding machine. For every composition, five samples were tested and the averages of the five measurements were reported.

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 (Zwick, Ulm-Germany). Heat deflection temperature (HDT) and Vicat softening point tests were done according to ISO 75 and ISO 307 standard with determined by CEAST 6521 (Ceast SpA Pianezza, Italy) HDT-Vicat test equipment.

The wear tests were done according to the DIN 53 516 method with Devotrans DA5 (Devotrans quality control test equipment, Turkey) abrasion test equipment (sand paper #60 and 0,32 m/s abrasion speed). The thickness of the test specimens was 7.0 mm and the diameter was 15.5 mm. Cylinder rotational speed was selected as 40 rpm and normal load (F_N) of 10N was used. Total sliding distance (L) was 40 m. The mass loss of the samples (Δm) was measured after the wear process and the specific wear rates (Ws) were calculated using the following equation:

$$Ws=(\Delta m)/\rho.F_N.L \ (cm^3/Nm) \qquad (1)$$

where Δm is the specimen's mass loss, ρ is the density of specimen, F_N is the normal load applied, and L is the total sliding distance. The friction coefficients and wear rates reported in the present study were the averages of three separate tests.

The fractured surfaces of the HDPE polymer composites were coated to thickness of 10-12 nm of a gold (Au) (80%)/palladium (Pd) (20%) alloys to prevent electrical charging by Polaron SC 7620 (Gala Instrumente GmbH, Germany). The surfaces of the prepared samples were observed by the JEOL-JSM 5910 LV (JEOL Ltd., Japan) scanning electron microscopy (SEM) at an acceleration voltage of 20 kV.

3. Result and discussion

The relationship between the elasticity modulus and the percentage of the filler of HDPE

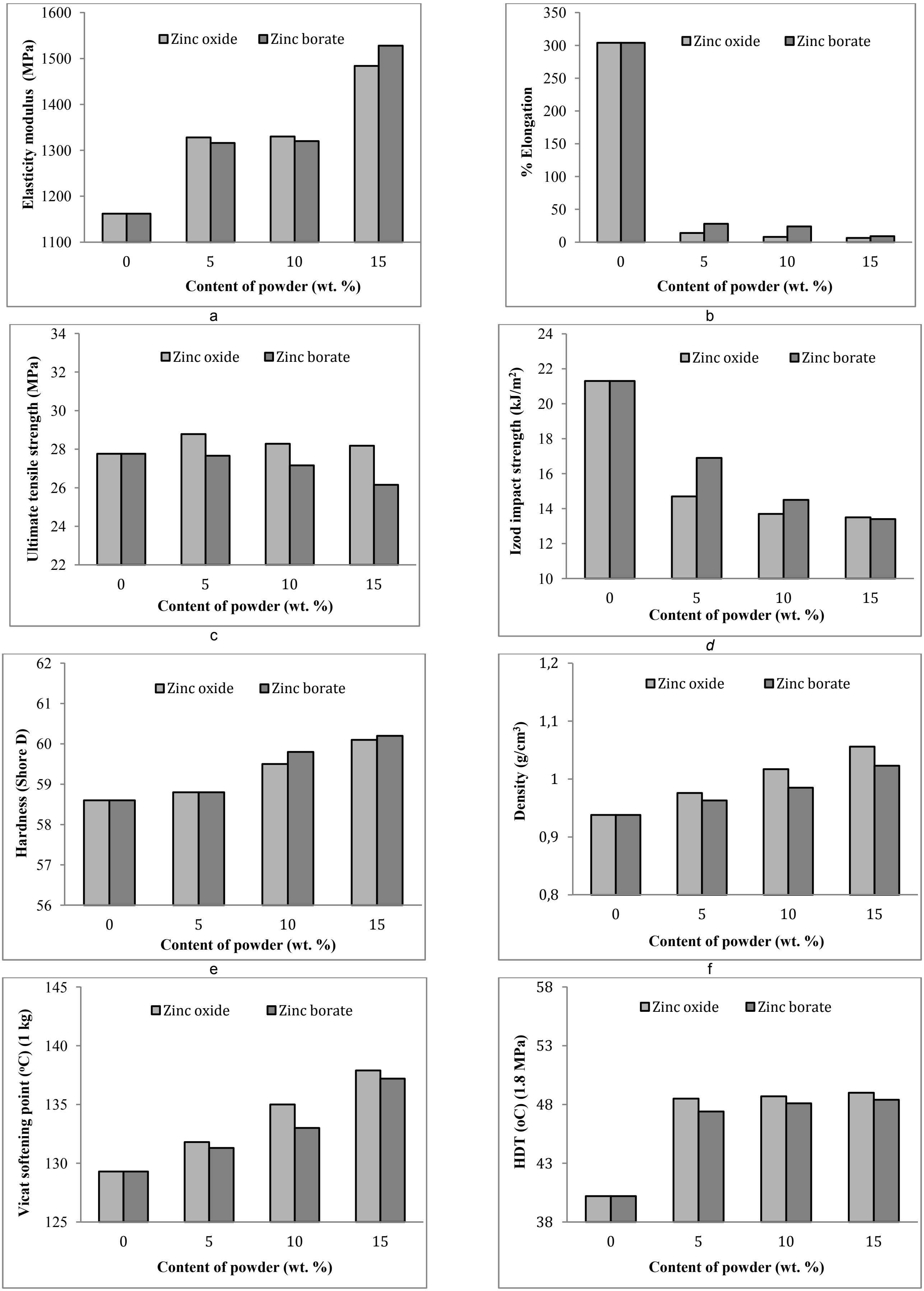

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Fig. 1 continues on next page

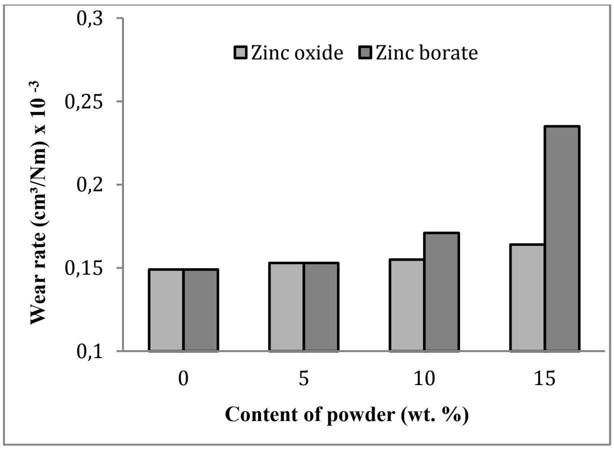

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Fig. 1 - Mechanical properties of the HDPE/zinc oxide-zinc borate polymer composites.

composites is shown in the Figure 1-a. The elasticity modulus of HDPE/zinc oxide and zinc borate composites increases as the zinc oxide and zinc borate concentration increases from 0 to 15 wt %.

The maximum elasticity modulus is observed at the 15 wt % zinc borate concentration for HDPE. In comparison with the elasticity modulus of virgin HDPE, the elasticity modulus increased by 33% for the composites with a 15 wt % zinc borate concentration. This observation is a clear indication that the addition of powdered filler into high density polyethylene matrix improves the stiffness of the polymer composite. The elongation at break of zinc oxide and zinc borate filled HDPE composites was measured, as shown in Figure 1-b. With increased loading, the elongation at break of composites filled with zinc oxide and zinc borate is decreased for all samples. The minimum elongation at break is observed at the 15 wt % zinc borate concentration for HDPE. The increase of the zinc oxide and zinc borate content in the HDPE matrix resulted in the stiffening and hardening of the composite which reduced its ductility and led to lower elongation property. The reduction of the elongation at break with the increasing filler content indicates the incapability of the filler to support the stress transfer from filler to polymer matrix [26]. The relationship between the ratio percentage of the zinc oxide and zinc borate and ultimate tensile strength of HDPE composites is shown in the Figure 1-c. The values of ultimate tensile strength decreased with increasing zinc oxide and zinc borate and, hence, zinc oxide and zinc borate does not improve the ultimate tensile strength of HDPE specimens prepared by compression molding. Addition of ZnO and $ZnHBO_3$ beyond 5 wt% decreased the ultimate tensile strength. This may be due to the aggregates of ZnO and ZnHBO3 particles in a polymer matrix increased with increasing ZnO and $ZnHBO_3$ content.

Figure 1-d illustrates the effect of zinc oxide and zinc borate on the Izod impact strength (notched) of HDPE composites. The impact strength decreased as the zinc oxide and zinc borate particle concentration increased from 0 to 15 wt %. The minimum Izod impact strength is observed at the 15 wt % zinc borate concentration for HDPE. In comparison with the Izod impact strength of virgin HDPE, the Izod impact strength decreased by 50 % for the composites with a 15 wt % zinc borate concentration.

The relationship between the zinc oxide-zinc borate content and the hardness of the HDPE polymer composites is shown in Figure 1-e. The hardness of the composites increased (from 0 to 15wt %) linearly with an increase weight percentage of zinc oxide-zinc borate. The maximum hardness is observed at the 15 wt % zinc borate concentration for HDPE. The specific gravity or density of polymer composites is a very important property that determines specific load application of the composite. This is because specific gravity or density has a direct relationship with the load bearing capacity of the composite as well as the cost [27]. The relationship between the zinc oxide-zinc borate content and the density of the polymer composites is shown in Figure 1-f. The density of the composites increased (from 0 to 15wt %) linearly with an increase weight percentage of zinc oxide - zinc borate. The maximum density is observed at the 15 wt % zinc oxide concentration for HDPE. The relationship between the Vicat softening temperature and the percentage of the filler of HDPE composites is given in the Figure 1-g. The Vicat softening temperature of HDPE/ zinc oxide and zinc borate composites increases as the zinc oxide and zinc borate concentration increases from 0 to 15 wt %. The maximum Vicat softening temperature is observed at the 15 wt % zinc oxide concentration for HDPE. On the other hand, HDT of HDPE/ zinc oxide and zinc borate composites show an increment as the filler concentration increases from 0 to 15 wt % (Figure 1-h). The zinc borate composite shows a lower Vicat softening temperature and HDT than the zinc oxide composites. At a larger zinc oxide and zinc borate concentration, the value of the HDT was not much changed. The values of zinc oxide and zinc borate content and wear rate relationship were obtained and are shown in Figure 1-i. By comparing with the HDPE without filler, it can be observed that the addition of 15 % zinc oxide and zinc borate increased the wear rate of the composites. Based on these results, it could be assumed that the level of the filler can affect the matrix hardness and bonding strength between the filler and polymer matrix. The weak bond led to the filler particles detaching from the matrix and the matrix pulling out more easily, which could increase the wear rate of the composite. So, a high level of the filler led to the high wear rate of the composite.

The morphology of fracture surfaces of impact specimens of HDPE/ZnO and $ZnHBO_3$ composites was examined by SEM. Figures 2 show the micrographs of the impact fracture surfaces of the composites filled with 5-15 wt% of ZnO and $ZnHBO_3$, respectively. It was observed that the dispersion of ZnO and $ZnHBO_3$ particles were relatively good and uniformly dispersed throughout the entire polymer matrix. However, at high ZnO and $ZnHBO_3$ contents, the ZnO and $ZnHBO_3$ particles may aggregate to each other to become a cluster of ZnO and $ZnHBO_3$.

4. Conclusions

Composites of HDPE with ZnO and $ZnHBO_3$ were prepared by melt mixing in a twin screw extruder. The HDPE composites showed an increased in elasticity modulus and hardness with increasing filler content. The increase of ZnO and $ZnHBO_3$ content in the HDPE matrix resulted in the stiffening and hardening of the composite which reduced its ductility, and led to lower elongation property. The dispersion of ZnO and $ZnHBO_3$ particles in a polymer matrix was investigated using SEM. Based on this examination, we infer that ZnO and $ZnHBO_3$ at low percentages distributed uniformly on the subsurface of the HDPE composite, which reduces the destruction of HDPE during wear process. Also observed, the higher percentages of reinforcing ZnO and $ZnHBO_3$ particles in the polymer matrix leads to aggregation.

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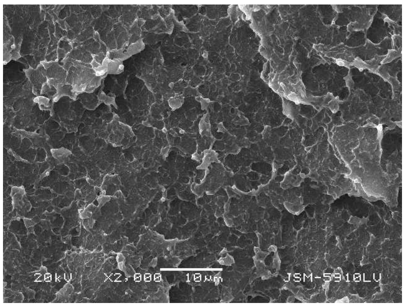
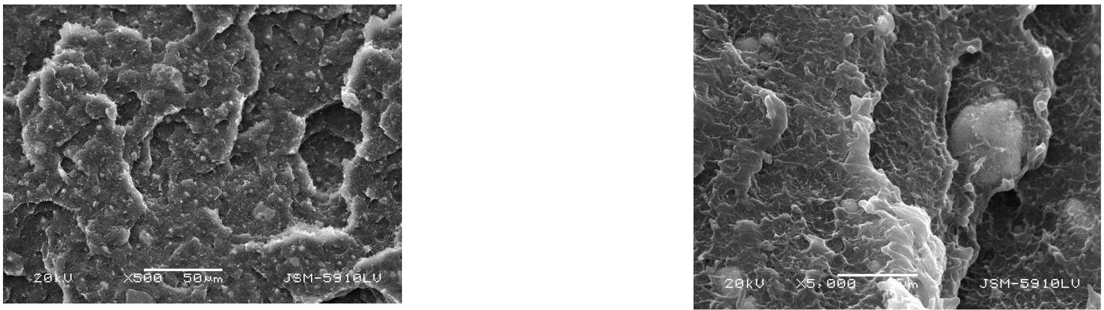


a -Pure HDPE



b -5wt% ZnO

c -15wt% ZnO

d -5wt % $ZnHBO_3$

e- 15wt % $ZnHBO_3$

Fig.2- SEM micrographs of HDPE/ZnO - $ZnHBO_3$ composites.

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