

PROPRIETĂȚILE MECANICE, MORFOLOGICE ȘI TERMICE ALE COMPOZITELOR POLIMERICE PE BAZĂ DE HDPE ARMATE CU TALC, CARBONAT DE CALCIU ȘI SFERE DE STICLĂ MECHANICAL, MORPHOLOGICAL AND THERMAL PROPERTIES OF HDPE POLYMER COMPOSITES FILLED WITH TALC, CALCIUM CARBONATE AND GLASS SPHERES

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Fillers, in the form of particulates and fibers, are often added to polymeric materials to improve their stiffness and strength. Polymers and their composites are being increasingly employed in view of their good strengths and low densities. Besides, a wider choice of materials and ease of manufacturing make them ideal for engineering applications. High density polyethylene filled with particulate fillers is of great interest in both research and industry. It is well known that HDPE has good process ability allowing accepting different types of natural and synthetic fillers. As fillers, mica, kaolin, calcium carbonate and talc are the most often used to reduce both the production cost and to improve the properties of the thermoplastics, such as rigidity, strength, hardness, flexural modulus, dimensional stability, crystallinity, electrical and thermal conductivity. In the present work, high density polyethylene based composites filled with glass spheres, talc and calcite particles were prepared. Filler contents in the HDPE were 5, 10, 15, and 20 wt%. HDPE composites filled with glass spheres, talc and calcium carbonate were prepared using extrusion compounding and injection molding. The effects of filler contents on the mechanical, morphological and thermal properties of the polymer composites were studied. The modulus of elasticity, yield and tensile strength, % elongation, Izod notched impact strength, Shore D hardness, MFI, HDT and Vicat softening point of the composites were determined. The structure and properties of the composites are characterized using a scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS).

Keywords: Mechanical properties, high density polyethylene, talc, glass spheres, calcite, polymer composites.

1. Introduction

Particulate inorganic fillers are commonly added to commercial thermoplastic resins for reasons of economy and also to favorably modify properties such as stiffness, heat distortion, and mouldability. However, there is usually a trade-off involved with other important properties, such as toughness and ultimate elongation, which are usually degraded. The minerals commonly used as fillers in plastic moulding compounds are calcium carbonate, alumina trihydrate, talc, mica, wollastonite, glass beads, silica, and clays [1]. 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 [2-5].

Due to its lamellar nature, the use of talc generally leads to a reinforcing effect in polymers. Two of the main uses of talc are as filler for polymers for use in vehicle applications and as filler with antiblocking properties in low and high density polyethylene [6,7]. Talc is a hydrated magnesium

silicate, $Mg_3Si_4O_{10}(OH)_2$, with a basal space of 0.96nm between the layers, formed from a central octahedral coordinated magnesium hydroxide in trioctahedral arrangement sandwiched between tetrahedral coordinated Si_2O_5 silicate sheets [8-10]. The surfaces of the layers contain oxygen atoms, giving rise to hydrophobic characteristics. Its extremely hydrophobic surface, when in finely ground state floats on top of water, makes it an excellent material for various applications such as paints, adhesives, sealants and other building products. Due to its high aspect ratio, talc is widely used in rubbers and plastics, such as polypropylene, polyethylene, nylon etc., to reinforce compounds and reduce costs [8-11]. Other applications are involved in paper, ceramics, fertilizers, animal feed, cosmetics and pharmaceuticals. Karrad et al. investigated influence of talc on the properties of composites with high density polyethylene and polyethylene/polystyrene blends. They reported that some of the mechanical properties of the talc filled HDPE and talc filled 75/25 HDPE/PS blend were deduced from stress-strain measurements [12]. Chen et al. studied that investigation of nano-talc as a filling material and a reinforcing agent in high density polyethylene (HDPE). Analyses of the

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reinforced HDPE nano-composite show significant improvement in its mechanical properties including, tensile strength (> 26 MPa), break elongation (< 1.1%), flexural strength (> 22 MPa), and friction coefficients < 0.11. The results demonstrate that, after surface-treated, talc can be used as a promising filling material and a reinforcing agent in making HDPE nano-composite [13].

Calcium carbonate is the second most widely used mineral filler after talc. The use of CaCO₃ with a suitable hardness (Mohr hardness ~3) does not cause short-term failure in processing machinery [14]. A lot of research works have been done to characterize calcium carbonate as filler. Calcium carbonate based fillers have extensively been used because of their low-cost and availability. Nowadays, the raw material industries supply many different kinds of engineered calcium carbonate particulates that are produced by chemical precipitation from calcium hydroxide. These particulates are often produced especially for using as filler in polymers [15]. 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, CaCO₃ is difficult to disperse and stabilize in a polymer matrix [16-19]. 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. [20] 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 [21]. 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.

The application of light weight fillers, in the form of hollow glass spheres, in plastics has become more and more important in the last few years as well. Nijenhuis et al. investigated of mechanical properties of PA-6/hollow glass spheres polymer composites [22]. Kubat et al. investigated that characterization of interfacial interactions in high density polyethylene filled with glass spheres using dynamic-mechanical analysis. In this study, The dynamic-mechanical properties of high density polyethylene filled with 20% by volume of untreated glass spheres or glass spheres treated with a silane-based coupling agent were studied as a function of temperature and imposed tensile deformation [23]. Smith et al. [24] reported synergistic toughening in a new type of hybrid-epoxy composite epoxy polymer modified by rubber particles and hollow glass spheres. The authors attributed the synergistic toughening to the multiplicative interactions between rubber particle cavitation/matrix shear yielding mechanisms and hollow glass sphere-induced microcracking as opposed to pinning or bridging mechanisms.

In this study, the effects of the talc, CaCO₃ and glass spheres 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 % glass spheres, talc and calcium carbonate were produced, and the properties of the composites were investigated.

Table 1

Composition of the different composite formulations (wt %)

Groups	HDPE	Glass spheres (Hollow)	Glass spheres (filled with alumina silicate)	Talc	Calcium carbonate
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	-
14	95	-	-	-	5
15	90	-	-	-	10
16	85	-	-	-	15
17	80	-	-	-	20

2. Experimental

2.1. Compositions and Materials

Seventeen different polymer composites were prepared. Compositions of HDPE polymer composites that were formed are given in Table 1.

High-density polyethylene (HDPE) (I 668 UV) was supplied by Petkim (Izmir-Turkey). Specific gravity is 0,970 g/cm³. Melt flow rate is 5.2 g/10 min (190°C–2.16 Kg). Yield strength is 28,0 MPa and notched Izod impact (23°C) is 12 kJ/m². Hollow glass spheres (CenTron) was supplied by RockTron International (Bristol- United Kingdom). Also, Glass spheres (filled with alumina silicate) (MinTron 7) was supplied by RockTron International (Bristol- United Kingdom). Its moisture content and particle specific gravity are <0.5 % and 2.2-2.4 g/cm³ respectively. Particle size distribution (d50) is 20-35 μm. Talc (Tital 10) was supplied Ankerpoort NV (Maastricht- Netherlands). Its density is 2.8 g/cm³. Particle size distribution (d50) is 4.7 μm and moisture content is 0.2 %.. Calcium carbonate (calcite- CaCO₃) nano powder (Calprec PR) was supplied by Cales de Llierca (Girona-Spain). Its purity is 98 %. Particle diameter is 50nm.

2.2. Composite Preparation

Glass spheres, talc and calcium carbonate were dried in a Yamato vacuum oven ADP-31 (Yamato/VWR Scientific Products, Japan) 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 polymer composites were produced between 180-220°C at 20-30 bar pressure, and a rotation rate of 25 rpm, with a Microsan extruder (Microsan Instrument Inc. Kocaeli - Turkey). L/D ratio is 30, Ø: 25 mm, Polymer composites were also dried in vacuum oven at 80°C for 24 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	110–140
Waiting time in mold (s)	-	15
Screw speed (rpm)	25	25
Mould temperature (°C)	-	40

2.3. 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, strength at break 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). Flow behavior testing of all the mixtures was done according to ISO 1133 standard with Zwick 4100 MFI equipment. 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 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). Six samples were tested in each set and the average value was reported.

3. Result and discussion

3.1. Mechanical properties of the glass spheres, talc and calcium carbonate filled HDPE

Mechanical properties of the HDPE polymer composites are given in Figure 1. The relationship between the elasticity modulus and the percentage of the filler of HDPE composites is shown in the Figure 1-a. The elasticity modulus of HDPE/Glass spheres (hollow) composites increases as the filler concentration increases from 0 to 20 wt %. The maximum elasticity modulus is observed at the 20 wt % talc concentration for HDPE. In comparison with the elasticity modulus of virgin HDPE, the elasticity modulus increased by 25% for the composites with a 20 wt % filler concentration. On the other hand, the elasticity modulus of HDPE/glass spheres (filled with alumina silicate) and calcium carbonate composites shows an increment as the filler concentration increases from 0 to 20 wt %. The results showed that the elasticity modulus of composites improved with increasing the fillers concentration. In a study on HDPE/PS/talc by Karrad et al [1] similar effects on the mechanical behavior were obtained. According to their study

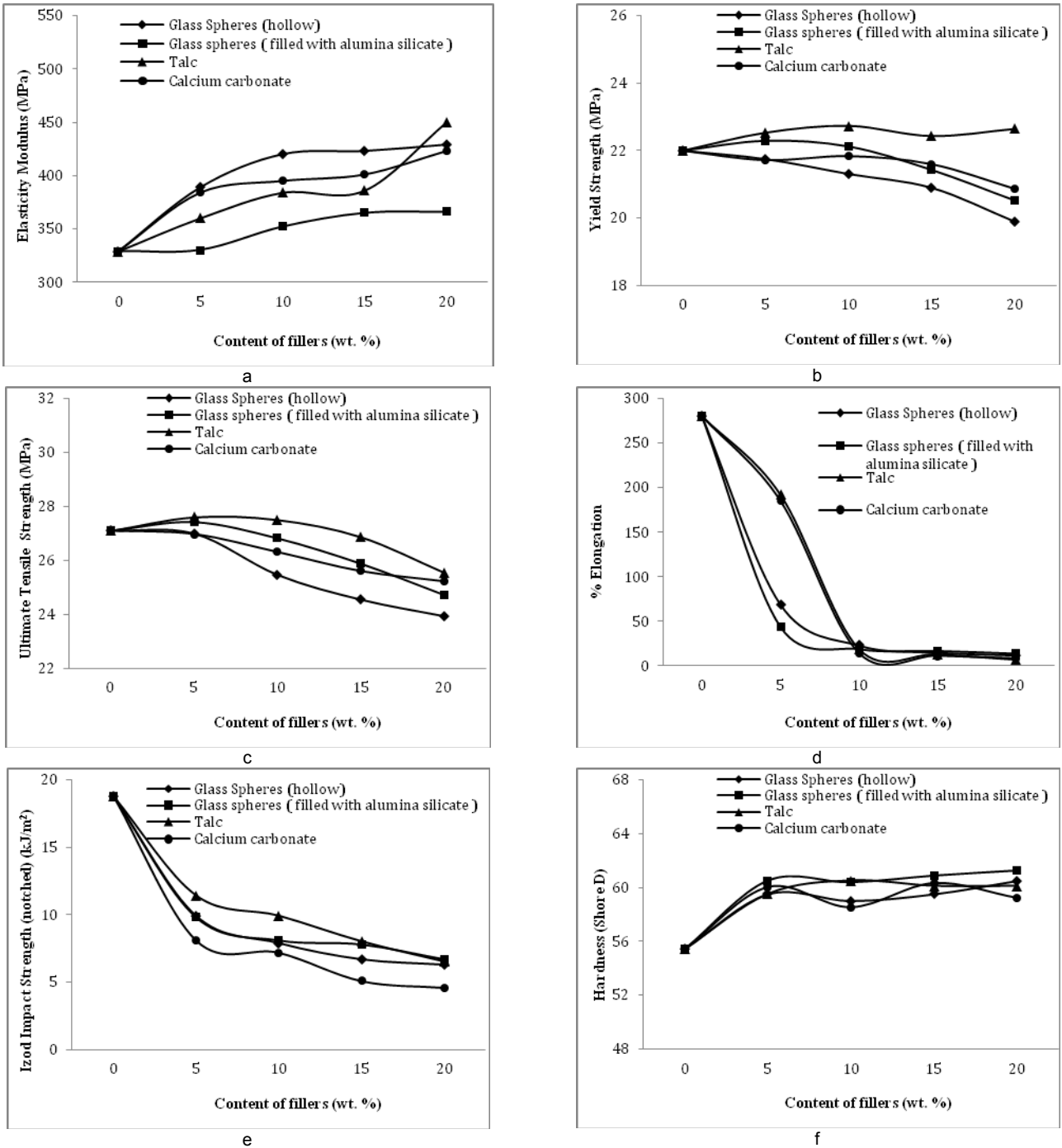


Fig. 1 - Mechanical properties of the HDPE polymer composites.

the modulus gradually increased with increasing talc content. The yield strength of glass spheres (hollow and filled with alumina silicate), talc and calcium carbonate filled composites were measured, as shown in Figure 1-b. The yield strength of the hollow glass spheres, glass spheres filled with alumina silicate and calcium carbonate composites decreased linearly with increasing filler content from 0 to 20 wt %. Subsequently, above 15 wt %, there was a reduction in the yield strength in glass spheres and calcium carbonate composites. But, the yield strength of HDPE filled with talc composites was not decreased. In a study on HDPE/CaCO₃ by Bartczak et al. similar effects on the mechanical behavior were obtained. According

to their study the yield stress and % elongation gradually decreased with increasing CaCO₃ content, while, Young's modulus increased in the blends with increasing concentration of CaCO₃ filler [25]. According to study of Suwanprateeb [26] on calcium carbonate filled polyethylene: correlation of hardness and yield stress, it was found that tensile yield stress decreased with increasing filler volume fraction whereas the compressive yield stress increased as the amount of filler was increased. In general, tensile properties of materials are largely determined by flaws and submicroscopic cracks. These flaws act as weak points in the materials. In contrast, the cracks do not play such an important role in

compression test because the applied stresses tend to close them rather than open them. Thus, compression properties tend to be characteristic of the pure polymer, while tension tests are more characteristic of the flaws in the material. Calcium carbonate–polyethylene composites are composed of rigid fillers dispersed in a ductile polymer matrix. These rigid fillers can act as defects in the composites if the filler is weak or the interface adhesion between fillers and matrix is not strong [27] which is the case for calcium carbonate–polyethylene composites in the present study.

The relationship between the ratio percentage of the filler and ultimate tensile strength of HDPE composites is shown in the Figure 1-c. Ultimate tensile strength of all composites shows a decrement as the filler concentration increases from 10 to 20 wt %. Above 10 wt % the results were not that good because the particles agglomerated at a higher percentage of talc and calcium carbonate composites. On the other hand, ultimate tensile strength of HDPE/glass spheres and HDPE/glass spheres (filled with alumina silicate) composites shows a decrement as the filler concentration increases from 10 to 20 wt%. In comparison with the ultimate tensile strength of virgin HDPE, the ultimate tensile strength decreased by 13% for the composites with a 20 wt % glass spheres (hollow) concentration. This decrease was attributed to a possible cracking of the hollow glass spheres.

The elongation at break of glass spheres (hollow and filled with alumina silicate), talc and calcium carbonate filled composites was measured, as shown in Figure 1-d. With increased loading, the elongation at break of the composites decreased for all. The minimum elongation at break is observed at the 20 wt % talc concentration for HDPE.

The study also focused on impact resistance behavior. As in the case of ultimate strain, a decrease in impact resistance is generally forecast in filled polymers. An exception may involve

ultrafine quasispherical fillers [28]. According to Bigg [29] all attempts to model the impact resistance of filled polymers are unsatisfactory. Figure 1-e presents the evolution of notched Izod impact resistance as function of glass spheres, talc and calcium carbonate fraction. A steady decrease can be noticed.

The relationship between the glass spheres, talc and calcium carbonate content and the hardness of the HDPE composites is shown in Figure 1-f. The hardness of the composites increased (from 0 to 5wt %) linearly with an increase weight percentage of glass spheres, talc and calcium carbonate. This was due to the uniform distribution of filler in the HDPE matrix. At a larger filler concentration, the value of the hardness was not much changed. The maximum hardness is observed at the 20 wt % glass spheres (filled with alumina silicate) concentration for HDPE. In comparison with the hardness of virgin HDPE, the hardness increased by 11% for the composites at a 20 wt % filler concentration.

3.2. Thermal and flow properties of the glass spheres, talc and calcium carbonate filled HDPE

Thermal and flow properties of the HDPE polymer composites are given in Figure 2. Figure 2-a and b illustrates the effect of glass spheres, talc and calcium carbonate on the Vicat softening point and HDT of HDPE composites. The Vicat softening temperature increased as the all particles concentration increased from 5 to 20 wt %. The maximum Vicat softening temperature is observed at the 20 wt % glass spheres (filled with alumina silicate) concentration for HDPE. On the other hand, the HDT value increased as the all particles concentration increased. The maximum HDT is observed at the 20 wt % talc concentration for HDPE. The relationship between the melt flow index (MFI) values and the percentage of the filler of HDPE composites is shown in the Figure 2-c. MFI values of all composites shows a decrement

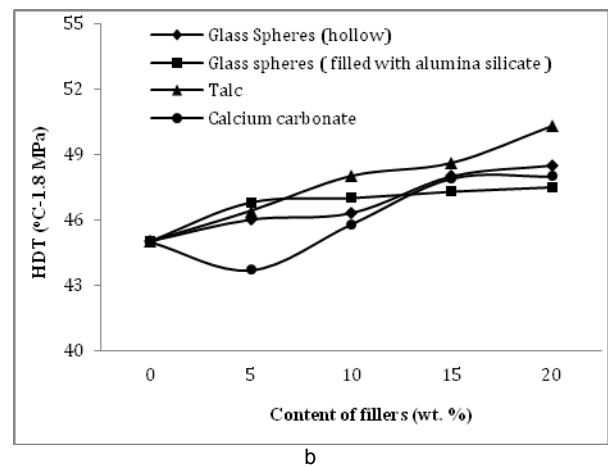
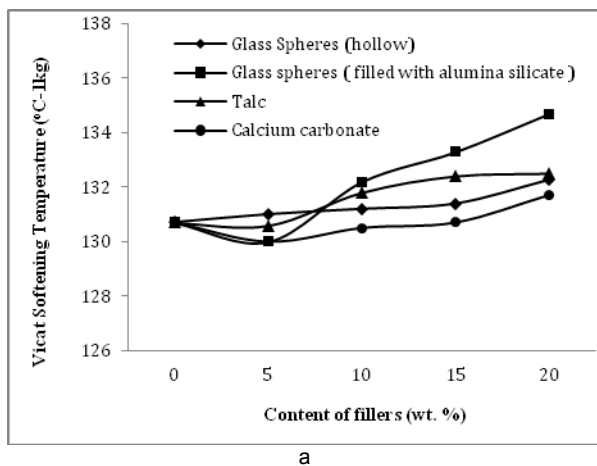


Fig. 2 - Thermal properties of the HDPE polymer composites

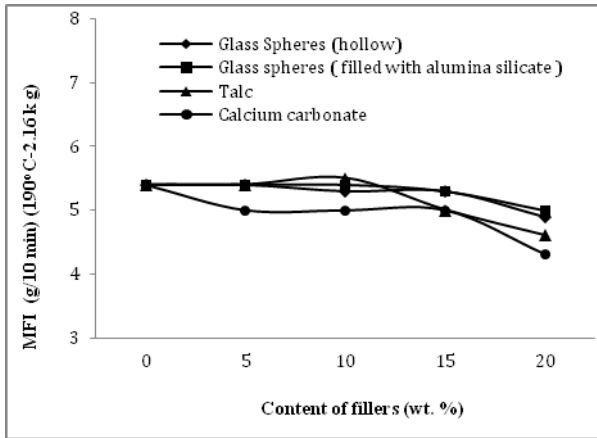


Fig. 2 Continue

as the filler concentration increases from 0 to 20 wt %. In comparison with the MFI value of virgin HDPE the MFI value decreased by 21% for the composites with a 20 wt % calcium carbonate concentration.

3.3. Morphological properties of the glass spheres, talc and calcium carbonate filled HDPE

The filler dispersion and the phase morphology of neat HDPE filled with various content 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.

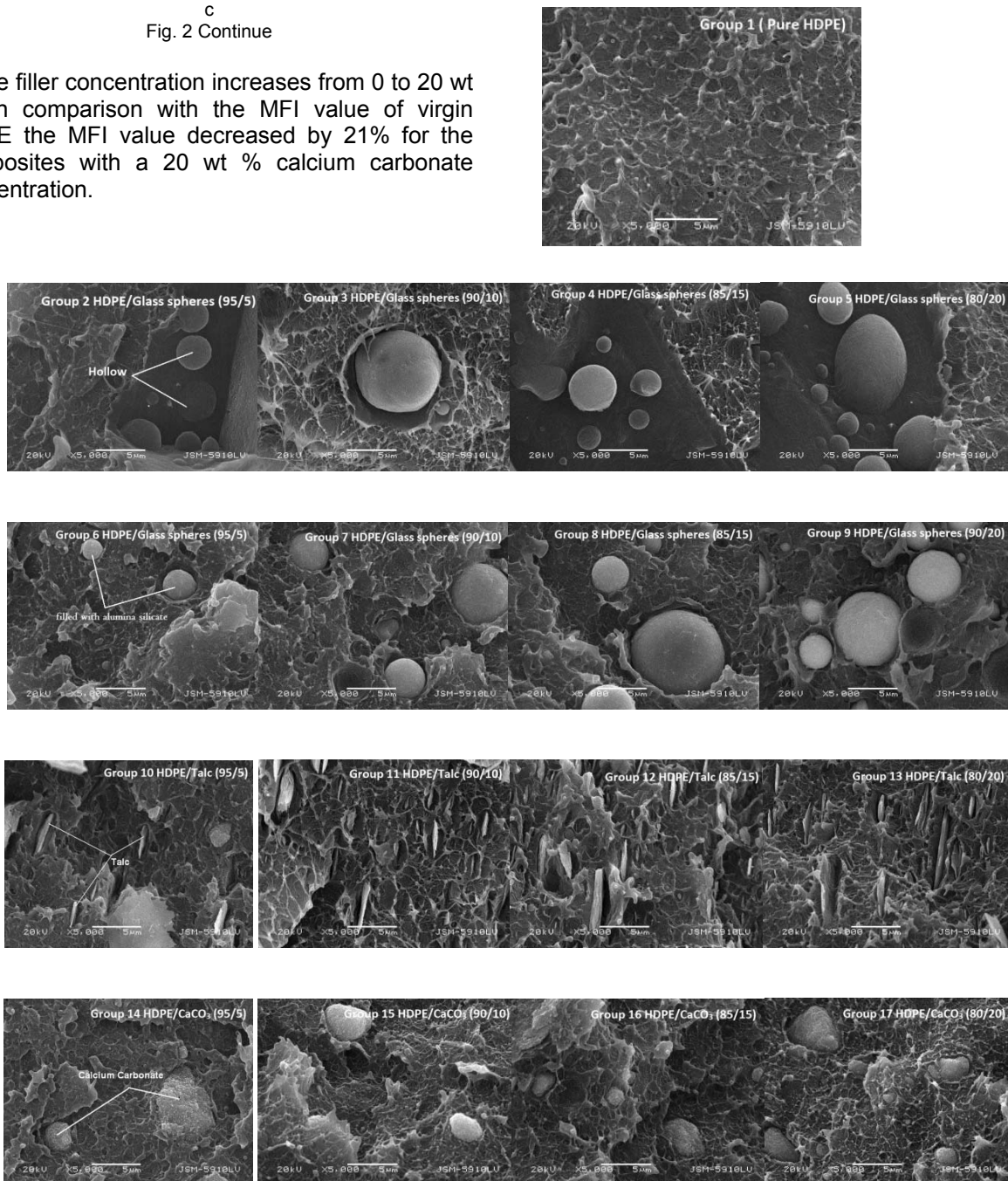


Fig. 3 - SEM micrographs of the HDPE polymer composites

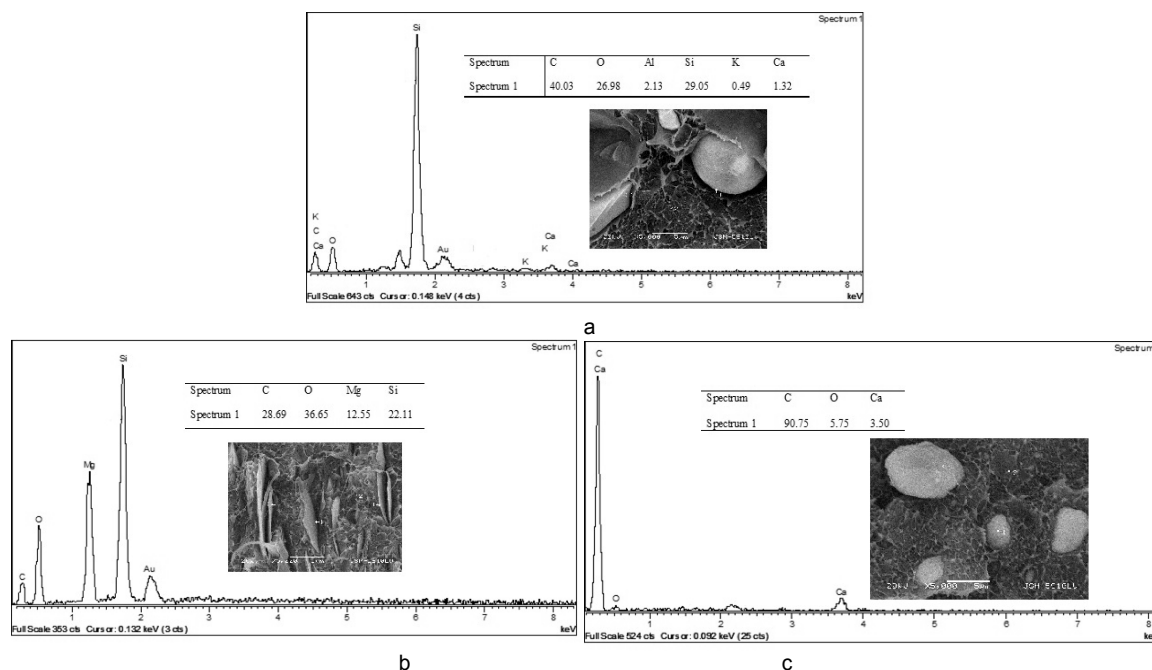


Fig. 4 - Energy dispersive X-ray spectroscopy (EDS) spectra of the polymer composites filled with: a. Glass Sphere; b. Talc and c. CaCO_3 .

The boundaries and the contrast can be obviously seen between the filler and HDPE matrix. The micrographs indicate that the all particulates are homogeneously dispersed on the fractured surfaces of polymer matrix. But, when the content of CaCO_3 particles reaches from 0 to 20 wt %, particle began to form agglomerates dispersed in HDPE matrix and this can be seen in Figure 3 (groups 14-17). The increasing severity of particle agglomeration at higher wt % accounts for the increasing deviations of the experimental values of the some mechanical properties of composites resulting from the poor adhesion between the agglomerate and polymer phases. The evidence of weak interface can be clearly observed from the SEM micrographs of the fracture surface of the composites after being tested in tension. The micrographs reveal the clean surfaces of talc [1], glass sphere and calcium carbonate [26] particles at the fracture surface without the presence of polyethylene layer. It means that polyethylene debonded completely from particles by breaking the interface. This results in the decrease in tensile yield stress with increasing filler content which corresponds to the increase in stress concentration and possible weak points with the increase in fillers volume fraction. During tensile loading, the interface between polyethylene and calcium carbonate is pulled apart. It was reported previously that tensile yielding of this type of composite was composed of interface and matrix yielding [26, 30].

4. Conclusions

The mechanical and thermo-physical properties of HDPE composites were investigated. Substantial improvements in the some mechanical properties were obtained by the addition of filler. For example, the results showed that the elasticity modulus of composites improved with increasing the filler content. This was due to the uniform distribution of filler in the HDPE matrix. Also, hardness, Vicat softening temperature and HDT values of composites improved with increasing the filler content. On the other hand, yield and tensile strength, % elongation, MFI values of the composites were decreased. This decrease was attributed to a possible agglomeration of the particles. Izod impact strength decreased as well. Fracture propagation was more pronounced with the addition of the particles. It is possible that talc and calcium carbonate particles agglomerated easily into large particles, which could be sites for crack propagation, and acted as a micro-crack initiator. However, at a larger filler concentration, the value of the impact strength was not much reduced.

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