USE OF GLASS FIBERS AND GLASS SPHERES TO IMPROVE MECHANICAL PROPERTIES OF HUNTITE AND HYDROMAGNESITE REINFORCED FLAME RETARDANT COMPOSITES

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In our previous studies, we observed excellent flame retardant properties of mineral reinforced polymer composites. However, it was investigated that some mechanical properties of the composites were deteriorated concurrently with adding minerals. In this study, it was aimed to improve those features by using glass fibers and glass spheres. Polyproplyene is used as a matrix material. Huntite hydromagnesite and glass fibers/spheres were embedded to the matrix in different loading levels. Prior to the composite production, crushing, grinding and screening processes were applied to the mineral. After fabrication of the mineral and glass fibers/spheres reinforced polyproplyene composite samples, they were characterized by using Scanning Electron Microscope - Energy Dispersive X-Ray Spectroscopy (SEM-EDS) to investigate the elemental analysis and morpology. Tensile and flexural tests were applied to determine the mechanical behaviours. Finally Flame retardancy test was undertaken to observe the flame retardant properties of the composites. It was concluded that the use of glass fibers is a beneficial way to improve mechanical properties of mineral reinforced flame retardant composites.

Keywords: *Flame retardant; Polymeric composites; Mechanical properties; Glass fibers; Glass spheres; Huntite hydromagnesite*

1. Introduction

Almost all of the plastic materials have hydrocarbon based structures which gives flammable property. This puts them into a dangerous situation because they are used in all areas of our lives. To get rid of this problem flame retardant additives are used in the plastic materials as a solution method to prevent casualties based on fire. They are embedded into the polymeric materials in an appropriate way, thus modification of plastic material is performed chemically or physically. The new plastic material can reduce the chance of fire and show resistance to ignition. Moreover, even if ignition starts, flame retardant additives act to delay the spread of flame, provide some extra time to extinguish and escape from area of fire [1-5].

Eventhough these additives vary widely within themselves, today can be divided into halogen-containing and non-halogen-containing ones. The use of halogen containing compounds has been reduced due to the detection of various harmful and toxic effects [6]. Ever then, the use of halogen-free additives began to gain importance. Inorganic minerals are at the head of this class; huntite and hydromagnesite minerals are ones of those. They are defined as natural mixtures having some useful filler properties for plastic applications. Huntite is calcium magnesium carbonate ($CaMg_3(CO_3)_4$), while hydromagnesite is hydrated magnesium carbonate ($Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$). The deposit, which has found important industrial use, normally consists of natural blends of these two minerals with varying ratios [2,6].

Regarding the mechanism of the flame retardant property, it can be said that the decomposition reaction of the minerals are assigned for the operation. The structures endothermically decompose at temperatures between 200 ^oC and 400 ^oC and liberate water steam and/or carbon dioxide. Besides the cooling effect and extinguishing of the flames by inert gases, the flame retardant effect is improved by formation of a kind of ceramic layer formed on the compound surface and this surface protects the ignitable materials from further attacks by flames and heat [6-8].

In addition to many advantages, halogen-free minerals have some limitations. They have to be added much larger quantities to get enough flammability compared to halogen-containing ones. In previous studies, we observed that this caused to deterioration in some mechanical properties which are essential to work as while composed materials are in service [9-11]. In this study, glass fibers and glass spheres have been used as auxiliary additives to defeat this worsening [12-15]. Prior to composite production, crushing, grinding and screening processes were applied to the mineral. Glass fibers and glass spheres were added to polyproplyene matrix in different loading level to see the content

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dependence. After fabrication of composite samples, they were characterized by using SEM-EDS to observe the elemental analysis and morpology. Tensile and flexural tests were applied to the specimens to determine the mechanical properties. Flame retardancy test was undertaken to observe the flame retardant properties.

2. Materials and methods

Polypropylene (PP) was used as a main polymer matrix, grade HJ325MO from Borouge, Austria with the melt flow index of 50 g/10 min (MFI; 230°C/ 2.16 kg) and density 0.910 g/cm^3. Natural huntite/hydromagnesite mineral were supplied from Isparta/Tırtar region in Turkey. Two types of glasses were used; glass fibers and glass spheres. BF 1000 Glass Fibers and GB 1000 Glass Spheres were supplied by Duratek A.S, Turkey. They have 1.54 g/cm^3 density, white colour and 400 ^{o}C of decomposition temperature.

In the production process, firstly huntite and hyromagnesite were comminutioned by Retsch RS 200 which is type of vibrator disc grinder machine. After grinding process, sieving was applied by Retsch/ AS 200 machine, at 50 amplitude for 8 hours. The main aim of sieving was got to sub 10 microns particles. Then mineral particles were heated by labelled Memmert furnace overnight at 70^{o}C to remove humidity.

Composite pellets were manufactured by twin-screw extruder branded Labtech in Budin-Akarca Industry and Trade Limited Company. Huntite hydromagnesite, glass fibers and glass spheres were blended during the feeding of the extruder. Zone temperature of the extruder was set between 185^{o}C and 220 ^{o}C. Diameter of the extruder machine is 20 mm and screw speed was adjusted 190 rpm. After this process, Labtech Enginerring Hydraulic Press machine was used to produce composite plates. Press was performed at two different temperatures; hot press at 180 ^{o}C and cold press at 25 ^{o}C. Firstly hot press was applied at 3 stages; 40 bar pressure for 240 seconds, 70 bar pressure for 210 seconds and 120 bar pressure for 210 seconds. After that, cold press was applied for 120 seconds. Coding and the descriptions of the produced composite samples are shown in Table 1.

To investigate of elemental and morphology of specimens, Scanning Electron Microscope (SEM) and Energy Dispersive X-Ray Spectroscopy (EDX) analysis were performed by Zeiss/Gemini Sigma 300 Vp machine by secondary electron detectors at 5.00kV. Before this analysis all samples were coated with gold for electron conductivity by Quorum/ Q 150R ES machine. SHIMADZU AGS-X 5kN tensile machine was used for tensile testing at room temperature with a crosshead speed of 50 mm/min. 3 point bending test was carried out according to standard of DIN EN ISO 178 in SHIMADZU AGS-X 5kn at a crosshead speed of 1mm/min. For observing flame retardant propert of the composites LOI test was undertaken. This test measures the minimum concentration of oxygen in a flowing mixture of oxygen that will just support flaming combustion of a material initially at room temperature. The sample is ignited and burns from the top downwards. The rating or oxygen index is expressed in terms of this volume percent oxygen concentration. According to the classification specifications, if the oxygen index is less than 24, the product is identified as flammable. 24 to 28 is limited flame retardant, and 29 to 34 is flame retardant. And above 34 is defined as extra flame retardant [16].

3. Results and discussion

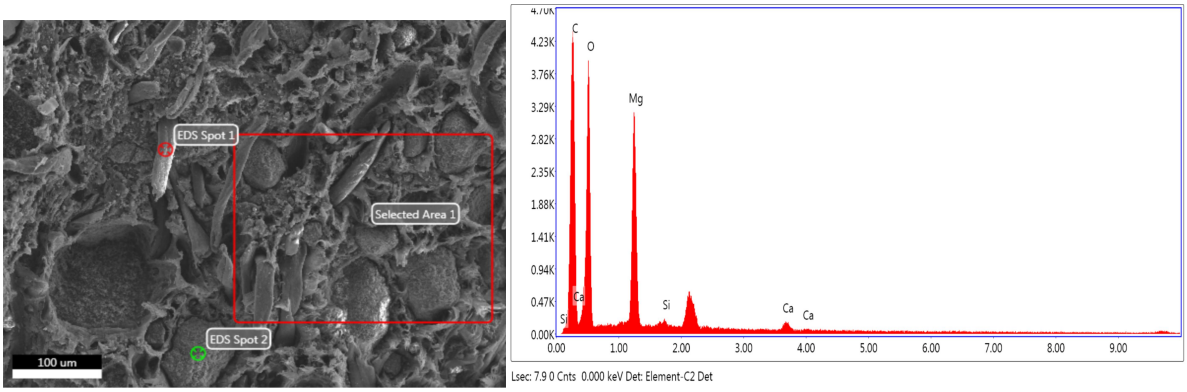
EDS scanning was performed to specimens of 0.5% fiber glass and sphere glass reinforced samples, the results can be seen in Figure 1. Mg and Ca elements which were related to huntite and hydromagnesite were detected and also Si element was identified in fiber/sphere glass reinforced composite due to SiO_2 formula of glass.

Figure 2, 3, 4 and 5 demonstrate the tensile and flexural tests results to determine the mechanical behaviours of the composites. All reinforced polypropylene composite samples have higher elastic modulus than pure polypropylene which has 1004 MPa (Figure 2). The sample of PH5F00G0, having only mineral additive as reinforcement, has 1550 MPa elastic modulus. By adding glass fibers with the ratio of 0.25%, 0.50%, 1%, 2% and 5% the elastic modulus increased to

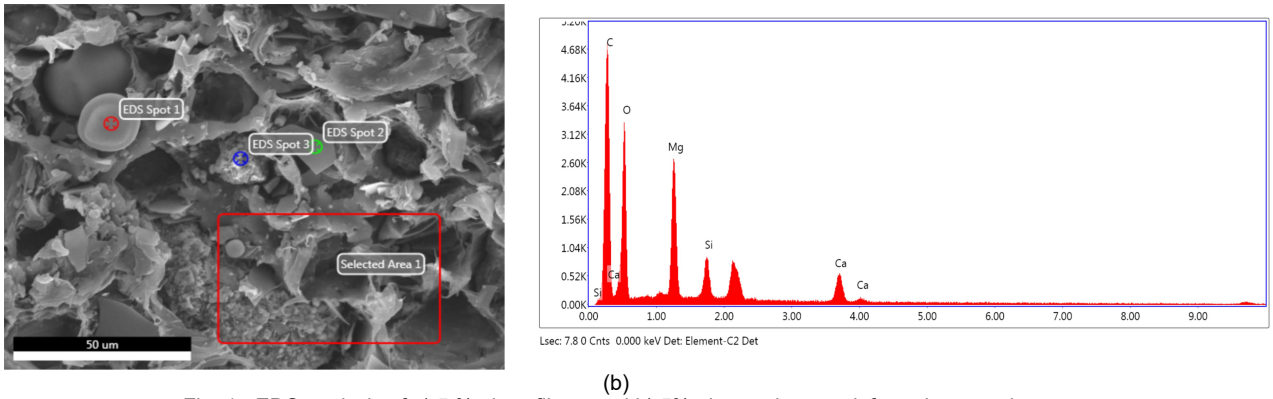
Table 1

Coding and the descriptions of the produced composite samples

Sample Code	Polypropylene	Huntite Hydromagnesite	Glass Fiber	Glass Sphere
PH0F00G0	100%	0	0	0
PH5F00G0	50%	50%	0	0
PH5F25G0	49.75%	50%	0.25%	0
PH5F50G0	49.50%	50%	0.50%	0
PH5F01G0	49%	50%	1%	0
PH5F02G0	48%	50%	2%	0
PH5F05G0	45%	50%	5%	0
PH5F0G25	49.75%	50%	0	0.25%
PH5F0G50	49.50%	50%	0	0.50%
PH5F0G01	49%	50%	0	1%
PH5F0G02	48%	50%	0	2%
PH5F0G05	45%	50%	0	5%

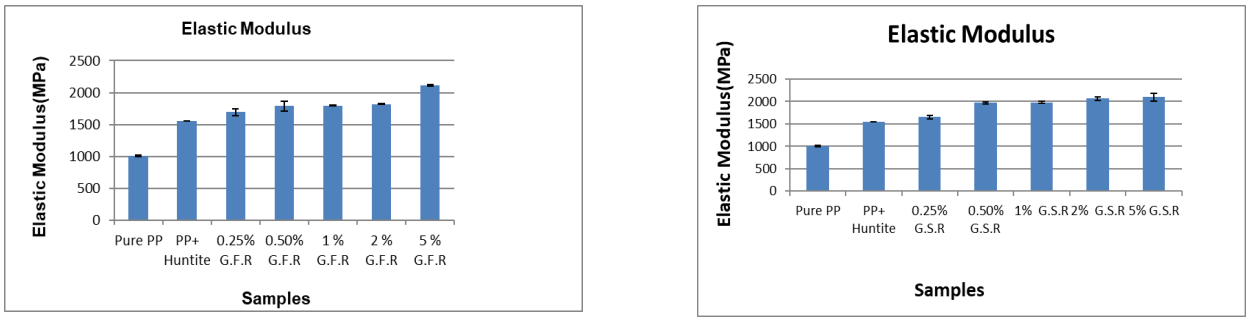


(a)



(b)

Fig. 1 - EDS analysis of a) 5 % glass fibers and b) 5% glass spheres reinforced composites.



a b

Fig. 2 - Elastic modulus of a) Glass fibers and b) Glass spheres reinforced composites.

1695, 1788, 1794, 1822 and 2111 MPa. Similarly, by adding glass spheres with the ratio of 0.25%, 0.50%, 1%, 2% and 5% the elastic modulus increased to 1654, 1972, 1982, 2069 and 2096 MPa. In fact, as we indicated in previous studies, there is no deterioration in the elastic modulus by adding mineral powders in the composites [9-11]. Moreover, elastic modulus was increased by adding glass fibers and spheres. The maximum elastic modulus was achieved as 2111 MPa by adding 5% glass fibers and 2096 MPa with %5 glass spheres.

Figure 3 depicts the tensile test results of the composites. Tensile strength of the pure polymer is 33 MPa. By adding mineral powder it is decreased dramatically to 14 MPa. This was observed from our previous study that the mineral powders decreased tensile strength [9-11]. The reason for this is poor compatibility between filler and polymer matrix. On the other hand, the plastic deformation of the polymer matrix and isolated filler particles are related to poor adhesion, which is directly related with the decrease of elongation for the samples with higher filler content. It can be cleary seen that when the glass fibers and spheres added to the composites, tensile strength values were improved. 0.25% glass fibers addition increased the tensile strength to 20 MPa. 0.5% and 01% glass fiber reinforced composites have 22 and 23 MPa tensile strength, respectively. However, after 1%, the tensile strength is decreased with 2% and 5% glass fiber content. This maybe related with the agglomeration of the fibers. The agglomerations cause disconnections and voids between fibers and the polymeric matrix. The reduction in the polymer phase leads to increase in phase separation.

Related with the sphere glass additive, similar results were obtained. The maximum tensile strength was achieved as 23 MPa with

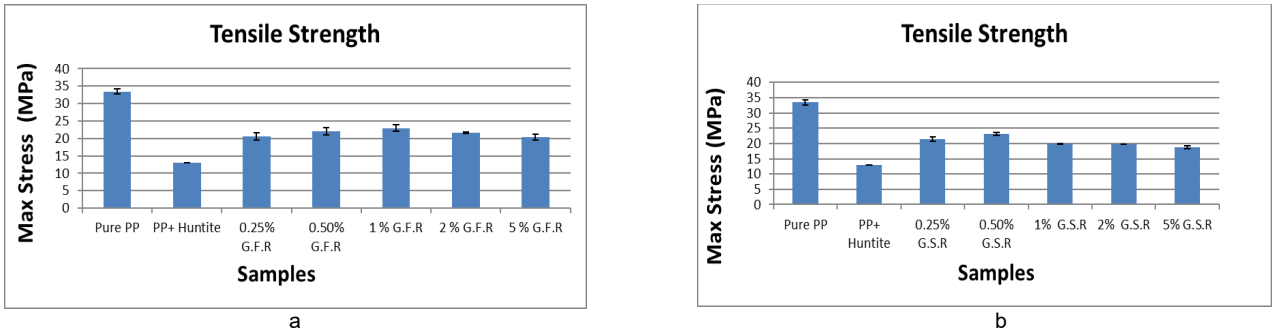


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Fig. 3 - Tensile strength of a) Glass fibers, b) Glass spheres reinforced composites.

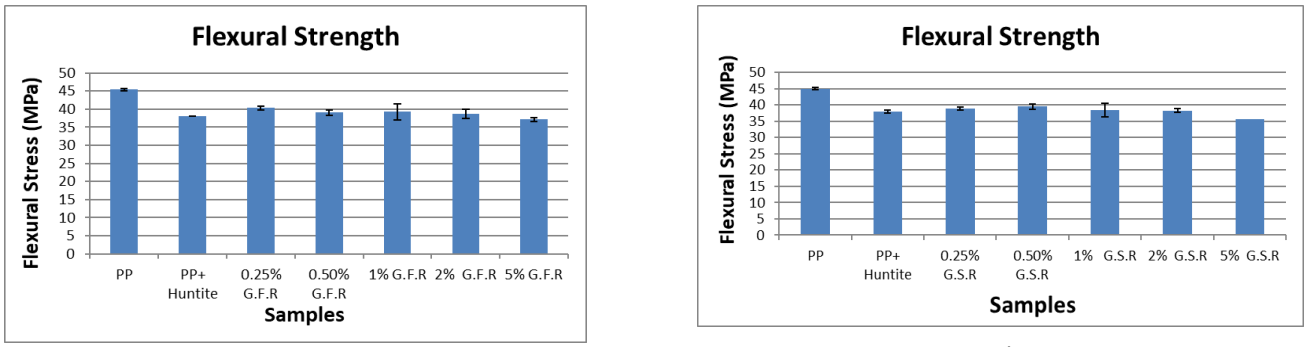

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Fig. 4. Flexural strength of a) glass fibers, b) glass spheres reinforced composites.

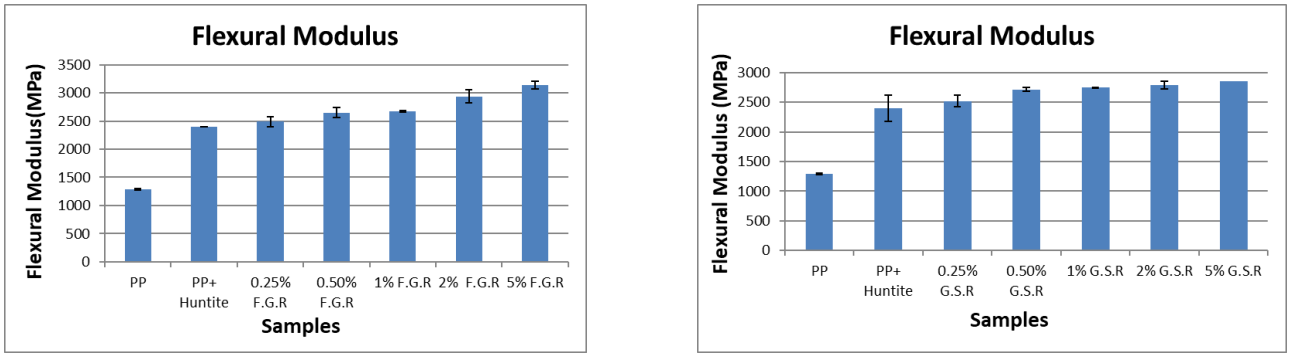

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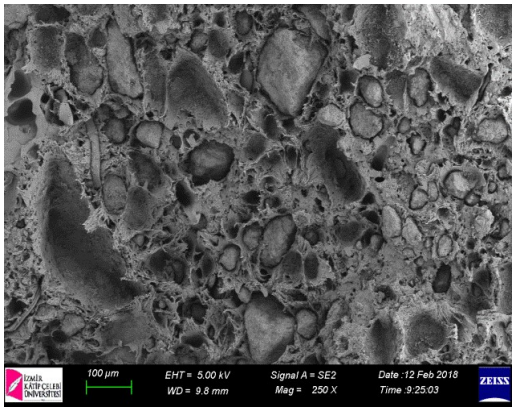
Fig. 5. Flexural modulus of a) glass fibers, b) glass spheres reinforced composites.

0.5% sphere glass reinforced polymeric composite. After this point, tensile strength decreased to 20 MPa, 20 MPa and 19 MPa with 1%, 2% and 5% glass spheres reinforced polymer composites, respectively. Similar to fiber glass addition, high amount of glass spheres decreased the tensile strenght. This is due to the aglomeration of the glass fibers and spherese. Polymer matrix, glass additives and mineral particles are separated during the loading of the mechanical test. Therefore, a relatively brittle fracture occurs. This phenomenon may be associated with the poor compatibility of the additives with polymer chains, reducing the tensile stress with an increase in additive content [12,17].

Flexural strength results obtained at the end of the 3 point bending test are demonstrated in Figure 4. Flexural strength of pure polymer sample is 45 MPa. Similar to tensile strength, adding of huntite and hydromagnesite decreased the flexural strength to 38 MPa. When we add glass fibers and spheres flexural strength values increased again. However, this improvement is not as high as tensile strength. Remarkable point is all flexural strength are close each other except pure polyproplyne specimen. The second highest flexural strength is 0.25% reinforced fiberglass with 40 MPa (Figure 4-a). The second group which is included reinforced sphere glass is shown figure 4-b. The lowest flexural strength is 36 MPa at 5% sphere glass reinforced poylmeric composite, while the highest flextural strength is 40 MPa at 0.5% sphere glass reinforced.

Another critical parameter for 3 point bending test is flexural modulus values. The flexural modulus was not deteriorated with mineral powders like elastic modulus. In contrast, adding huntite and hydromagnesite increased flexural modulus of the polymer from 1350 MPa, to 2400 MPa. Similar with the elastic modulus, glass fibers and spheres increased the flexural modulus. The maximum value is achieved as 3100 MPa with



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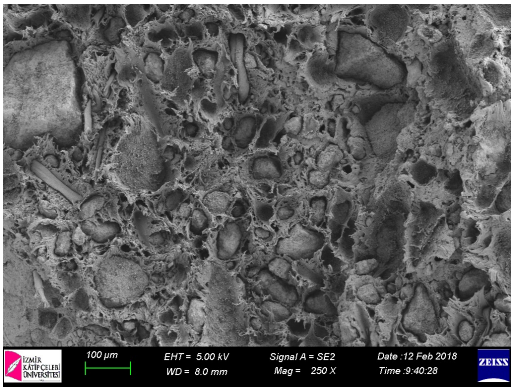

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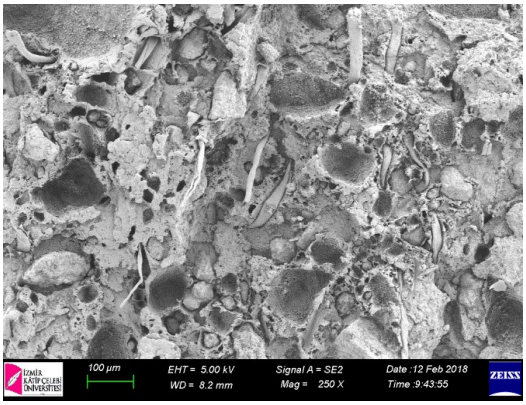

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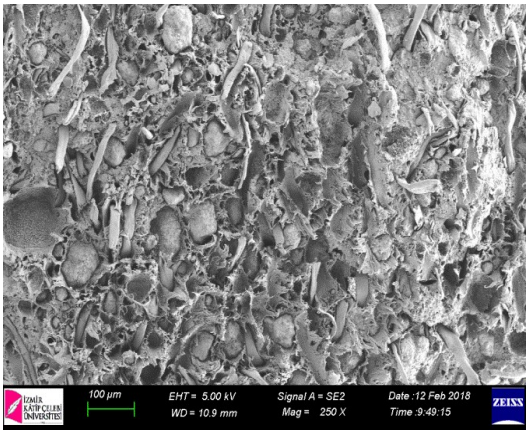

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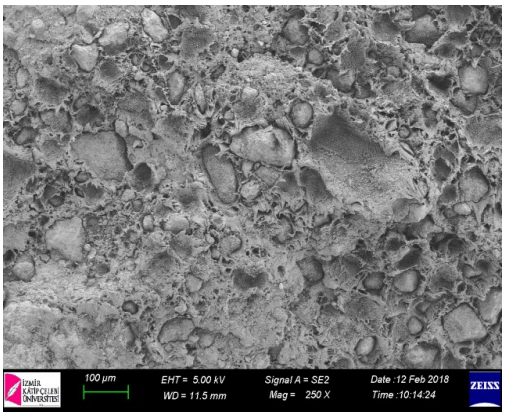
Fig. 6 - SEM images of glass fibers reinforced composite.



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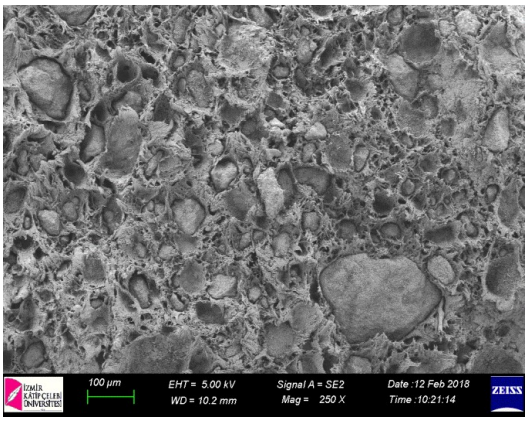

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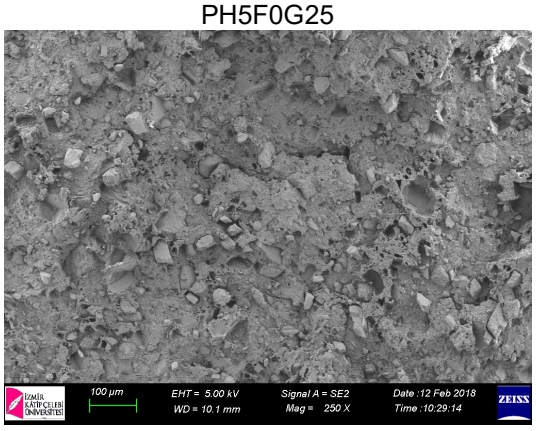

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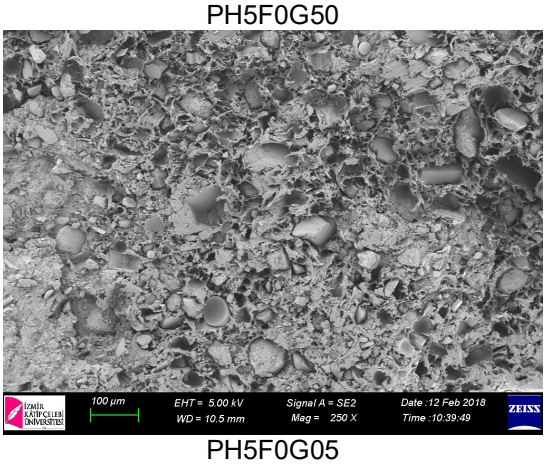

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Figure 7 - SEM images of glass spheres reinforced composite.

glass fibers, and 2750 MPa with glass spheres (Figure 5). So it can be said that glass fibers are more succesful in this area. It can be clearly seen; there is a linear increasing in both graphs. 5% fiberglass reinforced and 5 % spherical fiberglass reinforced composite have greatest flexural modulus with 3133 MPa and 2856 MPa, respectively.

Figure 6 and Figure 7 demonstrate SEM images of the composite fracture zones after mechanical tests. It can be seen that all additives clearly were seen in surface image. Structure of composite consisted of mineral particles and glass spheres or fibers surrounded by a polymer network. Regarding the morphology, huntite and hydromagnesite minerals have irregular shapes and consist mainly of aggregated ellipsoidal micelles structures. It was found that the dispersion of glass spheres and fibers in the matrix is roughly uniform. The gaps visible around the mineral additive indicate that there is a lack of bonding between the matrix and the additive. This explains the deterioration in mechanical properties when the mineral additives are embedded [13-15]. It is also seen that glass fibers are better bonded than spherical ones. It is explained in this way that the mechanical properties of the glass fibers reinforced composites are better than that of the spheres reinforced ones.

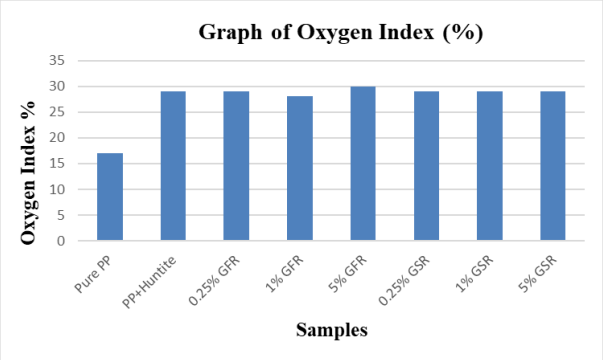

Fig. 8 - Flammability properties of samples.

Figure 8 depicts the measured oxygen index values of the composite samples. It can be easily seen that huntite and hydromagnesite minerals are effective in fireproofing. It is not surprising that this mineral makes polypropylene matrix fireproof. Such that, pure polypropylene initially had an oxygen index value of 17, but with the addition of minerals this value increased rapidly to 29. This has been proven in previous studies [6,17]. It was observed that this value did not change much in glass fiber or spheres embedded samples. The highest flammability performance was obtained in a 5% GFR sample having an oxygen index value of 30.

4. Conclusion

The main aim of this study is to improve the mechanical properties of mineral reinforced flame retardant composites. It can be said that the elastic modulus of the specimens were increased proportionally with fiberglass/sphereglass content. The highest elastic modulus value is 2111 MPa achieved with 5% fiberglass reinforced composite. The elastic modulus is 2096 MPa at 5% spherical fiberglass reinforced composite. At the end of the 3 point bending test it is resulted that pure PP has the highest flexural stress value with 45 MPa. The greatest flexural modulus is 3133 MPa which has 5% fiberglass reinforced composite. The strength of fiberglass reinforced composite was increased with increased fiberglass amount. Glass fibers are better bonded than spherical, this can be seen from SEM analysis. Thus, mechanical properties of fiberglass reinforced composites are better than the spherical reinforced ones.

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Data availability

The raw data required to reproduce these findings are available to download from [INSERT PERMANENT WEB LINK(s)]. The processed data required to reproduce these findings are available to download from [INSERT PERMANENT WEB LINK(s)].

REFERENCES

[1] R.N. Rothon. *Particulate Fillers for Polymers.* Rapra Technology Ltd, 2002, **9**, 10-17..

[2] G. Kirschbaum, Minerals on Fire, Flame Retardants Look to Mineral Solutions, *3rd Minerals in Compoundings Conference,* 8-10 April 2001.

[3] B. Toure, J.L. Cuesta, P. Gaudon, A. Benhassaine, A. Crespy. Fire resistance and mechanical properties of a huntite/hydromagnesite/antimony trioxide/decabromodiphenyl oxide filled PP-PE copolymer. Polymer Degradation and Stability, 1996, **53**(3), 371-379. DOI:10.1016/0141-3910(96)00100-0

[4] X. Wang, Y. Li, W. Liao, J. Gu, D. LĐ. A new intumescent flame-retardant: preparation, surface modification, and its application in polypropylene. Polymers for Advanced Technologies, 2008, **19**(8), 1055-1061. DOI:10.1002/pat.1077

[5] X. Qiu, Z. Li, X. Li, Z. Zhang. Flame retardant coatings prepared using layer by layer assembly:A review. Chemical Engineering Journal, 2018, **334**(2), 108-122. DOI:10.1016/j.cej.2017.09.194

[6] H.Y. Atay, E. Çelik. Use of Turkish huntite/hydromagnesite mineral in plastic materials as a flame retardant. Polymer Composites, 2010, **31**(10), 1692-1700.

[7] L. Haurie, A.I. Fernandez, J.I. Velasco, J.M. Chimenos, J.M. Lopez Cuesta, F. Espiell. Synthetic hydromagnesite as flame retardant. Evaluation of the flame behaviour in a polyethylene matrix. Polymer Degradation and Stability 2006, **91**(5), 165-174 DOI:10.1016/j.polymdegradstab.2005.08.009

[8] M.A. Oualha, N. Amdouni, F. Laoutid. Synergistic flame-retardant effect between calcium hydroxide and zinc borate in ethylene-vinyl acetate copolymer (EVA). Polymer Degradation and Stability, 2017, **144**(2), 315-324. DOI:10.1016/j.polymdegradstab.

[9] H.Y. Atay, E. Celik. Mechanical Properties of Flame-Retardant Huntite and Hydromagnesite-Reinforced Polymer Composites. Journal Polymer-Plastics Technology and Engineering, 2013, **52**(2), 182-188.

[10] Basfar A, Bae H.J. Influence of magnesium hydroxide (MH) and huntite hydromagnesite (HH) on mechanical properties of ethylene vinyl acetate (EVA) compounds cross-linked by dicumylperoxide and ionizing radiation. Journal of Fire Sciences, 2010, **28**(2), 161-180. DOI: 10.1177/ 0734904109340765.

[11] L.A. Savas, T.K. Deniz, U. Tayfun, M. Dogan. Effect of microcapsulated red phosphorus on flame retardant, thermal and mechanical properties of thermoplastic polyurethane composites filled with huntite&hydromagnesite mineral. Polymer Degradation and Stability, 2017, **135**(2), 121-129. DOI:10.1016/j.polymdegradstab.2016.12.001

[12] HY Atay. Improving mechanical properties and antibacterial behaviors of ceramic tile junctions with glass spheres and nano-Ag particles. Inorganic and Nano-Metal Chemistry, 2017, **47**(9), 1304-1311.

[13] A Zegaoui, M Derradji, A Medjahed, H Ghouti, A Hamid, W Cai, W Liu, A Dayo, Q Abdul, W Jun, Y Liu. Exploring the hybrid effects of short glass/basalt fibers on the mechanical, thermal and gamma radiation shielding properties of DCBA/BA-a resin composites. 2019, 10.1080/25740881.2019.1647237.

[14] YQ Li, SS Du, LY Liu, F Li, DB Liu, ZK Zhao, HM Xiao, N Hu, SY Fu. Synergistic Effects of Short Glass Fiber/short Carbon Fiber Hybrids on the Mechanical Properties of Polyethersulfone Composites. Polym. Compos. 2019, 40(S2), E1725-E1731. DOI: 10.1002/pc.25136.

[15] G Ojoc, P Catalin, S Simona, D Lorena. Glass fibers for impact protection systems. A review. IOP Conference Series: Materials Science and Engineering. 2019, 485. 012019. 10.1088/1757-899X/485/1/012019.

[16] M. Xanthos, Functional Fillers for Plastic, NY, Wiley-VCH (2004).

[17] HY Atay. Mineral takviyeli kablo tavalarının mekanik özelliklerini iyileştirmek için cam elyafların kullanılması. Ömer Halisdemir Üniversitesi Mühendislik Bilimleri Dergisi. 2017, **6**(1) 265-274.

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