PRODUCTION OF FLAME RETARDANT WOOD COMPOSITES BY USING HUNTITE AND HYDROMAGNESITE

Hüsnügül YILMAZ ATAY

İzmir Katip Çelebi University, Department of Material Science and Engineering, 35620 Çiğli İzmir Turkey

hgulyilmaz@gmail.com

Abstract: In this study, it is aimed to provide resistance to fire as seen the biggest obstacle to the wood that until 60-70 years of our lives in the almost forgotten today, even though it is frequently used in every aspect both as building material requirements of wood with furniture that we use in all areas of daily life, decorative items, in front of which is related to the use of the kitchen tools or for decoration. In this study, inorganic Turkish huntite and hydromagnesite mineral was used as an additive flame retardant material during the production of wood composite. Primarily for the production of composite material, the mineral was crushed and ground. Mineralogical structure was determined by XRF, XRD and SEM-EDS devices. Thermal behavior was observed by DTA-TG apparatus. UL-94 test apparatus was used to determine flame retardant properties of the wood composites. In the preparation of the composites, changing of the mineral additive rate was considered. In this way the additive amount dependence of fireproof composite was observed to evaluate the optimum amount of mineral.

Keywords: Wood, Composites, Flame retardant, UL-94.

Introduction

A porous, fibrous, and anisotropic material, wood is a versatile composite material containing cellulose, hemicellulose and lignin. Although it is one of the most important structural materials, it is almost forgotten in all kind of industries nowadays because of mainly its flammable property. In fact wood is an environmentally-friendly natural material and has many good properties such as good damping characteristics, thermal insulation, relatively low price and low specific gravity. In addition, wood can gain higher hardness, better weather resistance, abrasion resistance and higher strength by modification (Shah et al., 2017).

Porosity is another serious drawback of wood. The pores can interact with water due to the presence of hydrophilic groups present on its surface. Moreover the porous geometry provides channels for the flow of liquids and this which causes increased activity of microorganism in the presence of high moisture content and affects the dimensional stability of wood structures. Nevertheless, this may be converted to an advantage as the pores can be filled with the different functional materials (Shah et al, 2017; Leslaw, 2016).

The modification of wood is a topic that needs further investigations. Mostly modifications have been applied to the surface of the natural wood. This modified wood is effectively protected against degradation, has a higher life span and better mechanical properties compared to natural wood. Such as, a protective coating made of carnauba wax particles and zinc oxide was developed for the protection from both water and ultraviolet radiation (Lozhechnikova et al, 2017). In another investigation, hierarchical titania structures were constructed on wood followed by modification with perfluorodecyltriethoxysilane to produce a hydrophobic surface. Furthermore, a composite coating of titania/silica was also produced by hydrothermal process for the protection of wood (Liu et al, 2015). Shah et al. presented another method to render superhydrophobic properties to the wood (Shah et al., 2017).

In this study instead of modification of a natural wood, a wood composite was produced. This can be called engineered wood and includes a range of derivative wood products which are manufactured by binding or fixing the strands, particles, fibers, or boards of wood, together with adhesives, or other methods of fixation to form composite materials. Those products are used in a variety of applications, from home construction to commercial buildings to industrial products. They are engineered to precise design specifications which are tested to meet national or international standards (Oliveira, A.K.F. & d'Almeida, J.R.M., 2014).

Particle board is one of the engineering wood. It is manufactured from wood chips, sawmill shavings, or even sawdust, and a synthetic resin or other suitable binder, which is pressed and extruded. (Figure 1). Oriented strand board, also known as flakeboard, waferboard, or chipboard, is similar but uses machined wood flakes offering more strength. Particle board is cheaper, denser and more uniform than conventional wood and plywood and is substituted for them when cost is more important than strength and appearance (Taramian et al, 2007).

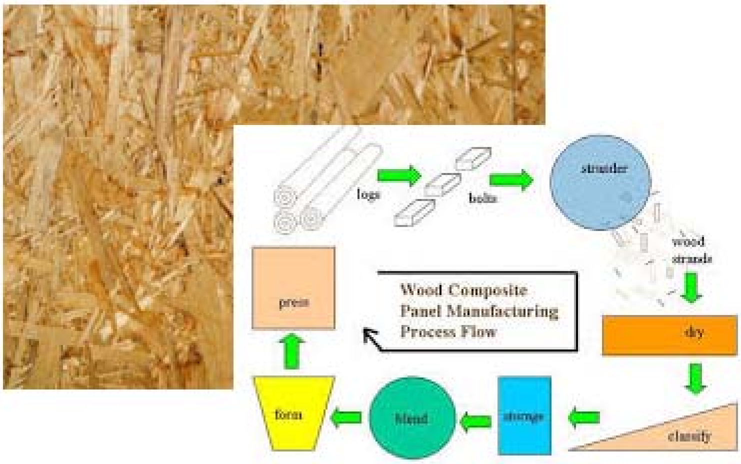


Figure 1. Particle board and munufacturing steps

As mentioned above that particle board are produced by using wood chips, sawmill shavings, or even sawdust. This is in fact an extremely important recycling process. The waste recycling covers several areas of interest such as environmental, engineering, economic and social and this is an important way to ensure sustainability in the world (Moreno, & Saron, 2017; Ng et al, 2014). The wood still is a material of expressive consumption for structural utilization for confection of furnishings, homes, buildings, among others. Packaging and pallets are also important products generated from timber industry. In Europe, around 20% of all sawnwood consumption is used for wooden pallets and packaging, while in Catalonia, northwest of Spain, 85% of the sawnwood is used to manufacture pallets. Conifers species such as pine are the main raw material for manufacture of the pallets (García-Durañona et al, 2016). The use of the pine presents an import environmental advantage due to their source from reforestation. The pine pallets are continuously submitted to high mechanical stress during use that of course lead to the usual break of the structural parts, disabling the entire pallet and generating pine waste wood (Moreno, & Saron, 2017).

A recycled wood composite was manufactured in this study by using huntite and hydromagnesite mineral additives to gain flame retardant property. The term flame retardant subsumes a diverse group of materials which are added to the materials, such as plastics and textiles, and surface finishes and coatings. Flame retardants inhibit or delay the spread of fire by suppressing the chemical or physical reactions in the flame or by the formation of a protective layer on the surface of a material. They may be mixed with the base material (additive flame retardants) or chemically bonded to it (reactive flame retardants) (Haurie et al, 2006; Le Bras et al, 2005). Both Reactive and Additive Flame retardant types can be further separated into several different classes, however two main categories can be seen as following; halogenated and halogen-free flame retardants. Halogen containing flame retardants act in the gas phase and contribute to incompletely burned substances like black smoke and toxic CO which is a highly toxic and nonirritating gas. As CO blocks the oxygen transport of the blood, it can disturb the respiration process immediately. Even though traditional solutions based on halogens have some advantages like low loadings and good retention of mechanical properties, they have also disadvantages compared to mineral flame retardants. Halogen free flame retardants are mostly inorganic fillers used to impart flame retardancy. Most used ones are alum, antimony trioxide, borax, chalk, magnesium oxide or silica. These fillers are usually cheap and in many cases help to improve the mechanical properties and surface appearance of the fabricated article (Kulshreshtha, 2002; Yılmaz Atay & Çelik, 2010).

Huntite and hydromagnesite mineral, one of the flame retardant mineral, has been used as an additive in the production of polymer composites to achieve incombustible property due to its inflammability property. The deposit normally consists of physical blends of two minerals huntite and hydromagnesite with varying ratios in between 40 and 30% huntite and 60 and 70% hydromagnesite The level of impurities is very low, the most important ones are other white carbonate minerals such as aragonite, calcite, and dolomite. Physical densities of huntite ($Mg_3Ca(CO_3)_4$) and hydromagnesite ($Mg_4(OH)_2(CO_3)_3.3H_2O$) minerals are 2.70 g/cm3 and 2.24 g/cm3, respectively (Yılmaz Atay & Çelik, 2010) . Although this mineral is said to be relatively new as it has entered into the market in 1980s, there are numbers of studies can be seen regarding huntite and hydromagnesite mineral used in polymer composites. However, there are no such studies related with the usage in wood composites.

This study investigated flame retardant behaviors of inorganic mineral huntite and hydromagnesite in wood composites. Primarily for the production of composite material, the mineral was crushed and ground. Mineralogical structure was determined by XRF, XRD and SEM-EDS devices. Thermal behavior was observed by DTA-TG apparatus. Flame retardant property of the wood composites was evaluated by UL-94 test. In the preparation of wood composites, the mineral was added to be used as additives during the production of wood materials. The samples were obtained by changing the mineral additive rate.

Materials and Methods

Fabrication of Composite Materials

The material is received from Isparta region in Turkey. Crushing and grinding steps were performed in Muğla Sıtkı Koçman University Department of Mining Engineering. Grinding was repeated in İzmir Katip Çelebi University Materials Science and Engineering Department with a ball mill to get finer particle size. Mixed and a well representative sample was drawn in each case for detail characterization and beneficiation studies.

Flame retardant wood composites were prepared by reinforcing mineral powders at different ratios into the sawdust. After well-mixing the determined amount of powders and sawdust, each mixtures were moulded under 3 tons of pressure using by a molding machine for preparation of the specimens. Each specimen has 10 mm diameter. Obtained samples and their descriptions are shown in Table 1.

Table 1. Sample codes and descriptions

Sample code	Huntite and Hydromagnesite amount in the mixture (%)
W00H	0
W20H	20
W25H	25
W30H	30
W35H	35
W40H	40
W45H	45
W50H	50
W55H	55
W60H	60

Characterization

A laser diffraction machine from Malvern Instruments, Mastersizer 2000 was used to obtain the particle size distribution of huntite hydromagnesite mineral powders. The thermal behaviors of hydromagnesite and huntite mineral and obtained composite materials were evaluated to observe decomposition and phase formation at a heating rate of 10 ^{0}C/min in the temperature range of 25–700 ^{0}C under air atmosphere by using DTA/TG machine Perkin Elmer. XRF studies were carried out for the identification of mineral phases present with an X-Ray Diffractometer (Amatek Spectro IQII) X-ray diffractometer in İzmir İnstitute of Technology. XRD analysis was performed on a Bruker D2 Phaser system with Ni-filtered Cu-K alpha radiation (k = 1.54 Å). SEM micrographs and EDS analysis were taken with Qanta Feg 250 SEM device with 3 kV accelerating voltage. Flame retardancy tests of the composites were performed by UL 94 technique with the machine of ZLT-ZYS Needle-Flame Tester. The material is conducted to the flame in a specific angle and distance. Extinguishing time of the flame and dripping ability are measured. Set-up of the experiment is shown in Figure 2.

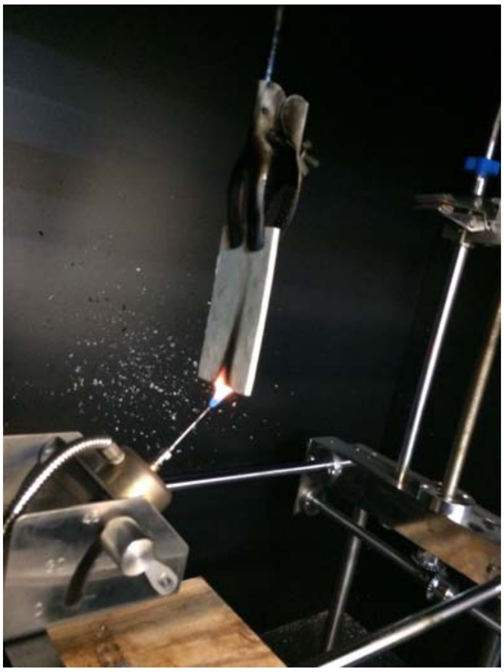


Figure 2. UL-94 flame retardant test experiment.

Results and Discussion

According to X-ray Fluorescence Spectrometry the chemical analysis of the mineral powder is as following; 53.32% Mg, 7.43% Ca, 0.53 Mn, 0.2 Al, 0.2 Ba, 0.1 Fe and 88.42% MgO, 10.4% CaO, 0.4 Al2O3, 0.07 MnO, 0.15 Fe2O3, 0.2 Ba. This results support XRD analysis and also literature information regarding chemical formula of huntite and hydromagnesite and impurities (Kirschbaum, 2001).

To determine the particle size Mastersizer 2000 the size distribution analysis is performed. The size distribution of the three particle sizes is shown in Figure 3. According to this analysis it can be said that mineral particle size is apprx. 10 μ.

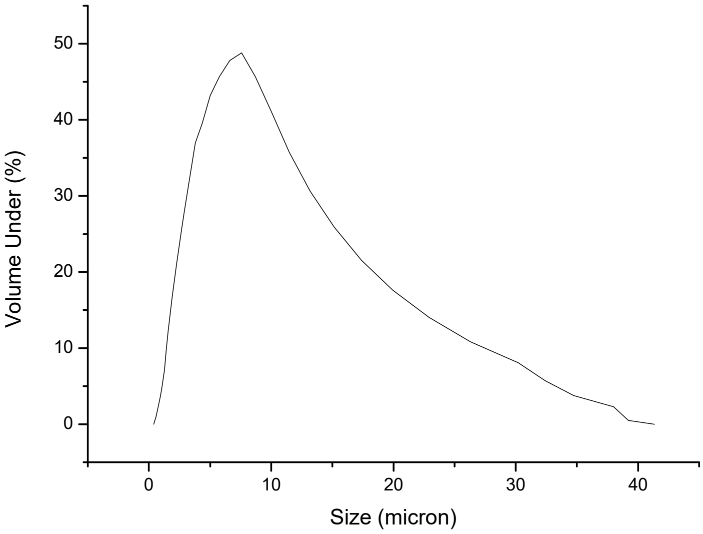


Figure 3. Size distribution of the mineral.

XRD analysis of the received material is shown in Figure 4. It is found from this result that the basic minerals are hydromagnesite (Mg(CO3)3.3H2O) and huntite (Mg3Ca(CO3)). Magnesite exists as the main impurity in the ore. And the other impurities can be counted dolomite and calcite. The main phases with high intensity are huntite and hydromagnesite. XRD analysis result promotes literature information which stated that the impurities magnesite, aragonite, and calcite phases are accompanying with huntite and hydromagnesite (Kirschbaum, 2001).

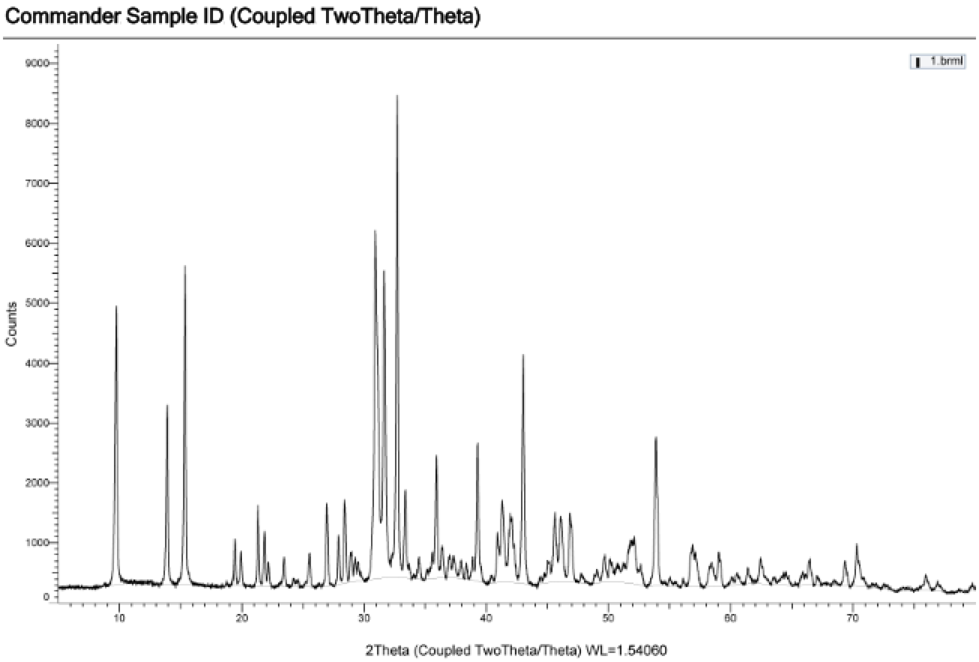


Figure 4. XRD analysis of the as-received material

Figure 5 demonstrates SEM micrographs and EDS analysis of huntite hydromagnesite mineral particles are shown in Figure 6. It is clearly seen from that the mineral particles are not circular but they are lateral with irregular shapes. EDS analysis supports XRD result as in the elemental analysis the elements of Mg, Ca, C, and O were indicated. There seem no any other elements as impurities.

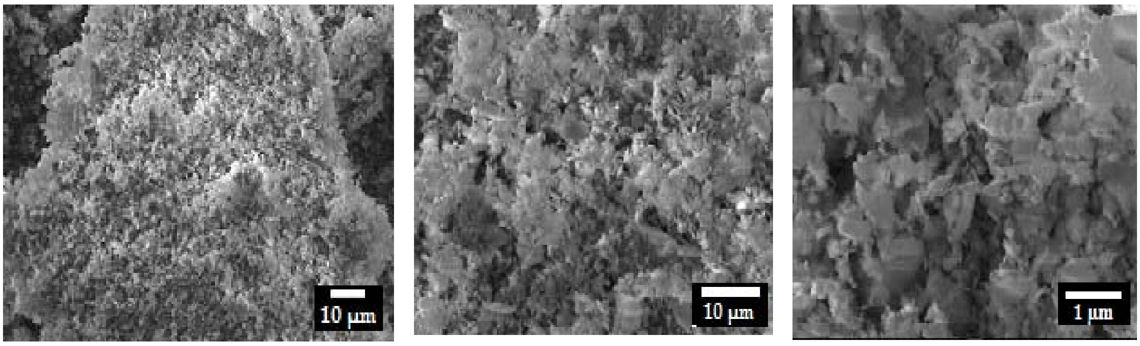
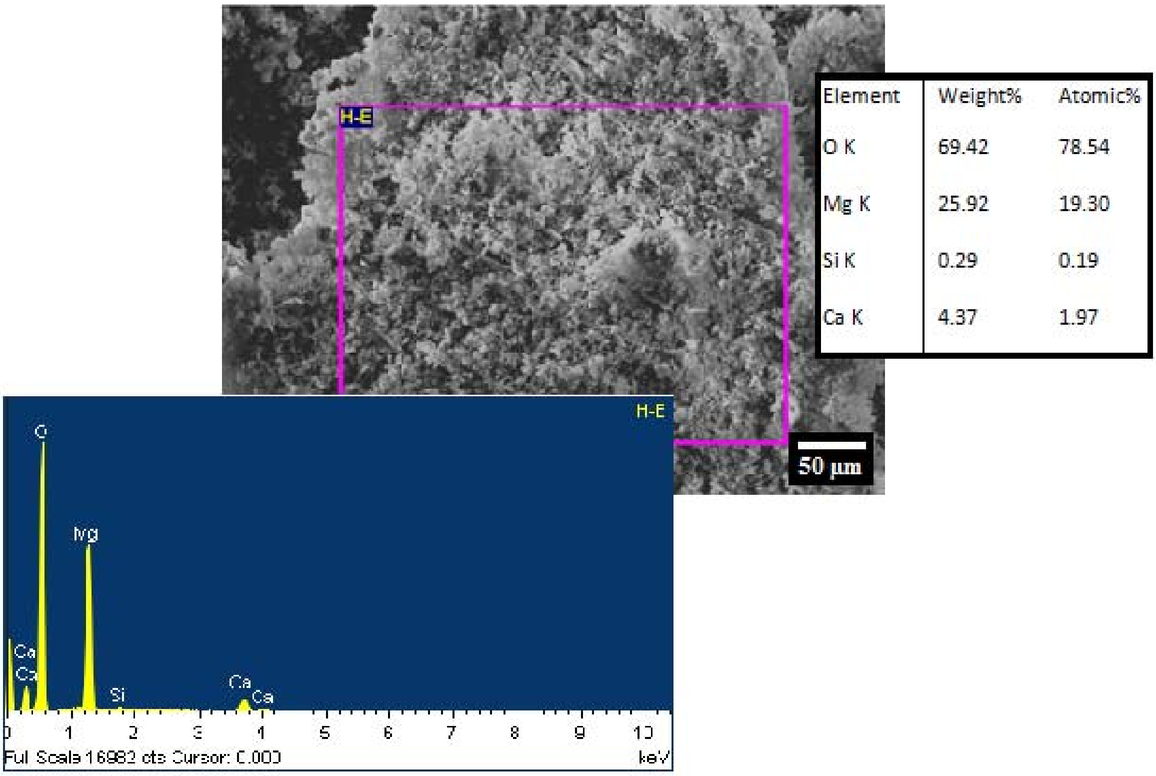


Figure 5. SEM micrographs of huntite and hydromagnesite



Element	Weight%	Atomic%
O K	69.42	78.54
Mg K	25.92	19.30
Si K	0.29	0.19
Ca K	4.37	1.97

Figure 6. EDS analysis of huntite and hydromagnesite

For the flame retardant property exothermic and endothermic reactions are important, thus DTA-TG analysis are carried out to huntite hydromagnesite mineral (Figure 7). This analysis was performed by heating up at the rate of 10 ºC/min at temperatures between 25ºC and 600ºC under air. Huntite and hydromagnesite have $Mg_3Ca(CO_3)_4$ and $Mg_4(OH)_2(CO_3)_3.3H_2O$ chemical formulas, respectively. Decomposition occurred in these minerals at temperatures between 25ºC and 600ºC. The first thermal phenomenon starts at 219.86ºC and ends at 331.89ºC and then heat absorption is -3,61 J, corresponding to removal of water and OH groups. After removal of water from hydromagnesite, $Mg_4(CO_3)_3$ decomposes to MgO and CO_2. It is estimated that the decomposition of $Mg_4(CO_3)_3$ occurs at temperatures between 376.29ºC and 490,76ºC This is the second thermal behaviour and heat absorbed at -5,49 J. It is difficult to separately state decomposition phenomena of the individual components of huntite hydromagnesite because it is a mixture of $Mg_4(OH)_2(CO_3)_3.3H_2O$ and $Mg_3Ca(CO_3)_4$. Finally the third thermal effect starts at 503.94ºC and ends at 598.29ºC. In this case, heat absorption is -1,43 J. MgO and CaO are formed by the end of this process. According to Equations 1 and 2, $Mg_4(OH)_2(CO_3)_3.3H_2O$ and $Mg_3Ca(CO_3)_4$ starts to decompose at high temperatures.

$$Mg_4(CO_3)_3(OH)_2.3H_2O \rightarrow 4MgO + 3CO_2 + 4H_2O \qquad (1)$$

$$Mg_3Ca(CO_3)_4 \rightarrow 3MgO + CaO + 4CO_2 \qquad (2)$$

By comparing TGA analysis was to evaluate thermal stabilities of huntite/hydromagnesite mineral. It can be seen from Figure 4b that the decomposition of huntite hydromagnesite mineral occurs at temperatures between 400 ºC and 500 ºC. The weight losses were resulted at those intervals, it is indicated that weight losses of huntite hydromagnesite mineral was estimated 56 wt.%.

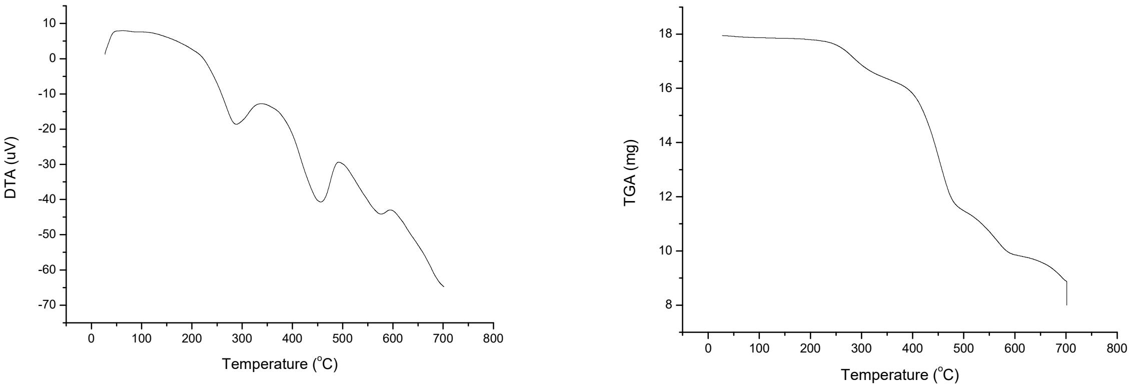


Figure 7. DTA and TGA curves of huntite hydromagnesite mineral.

Figure 8 and Figure 9 demonstrate SEM and EDS analysis of huntite hydromagnesite reinforced wood composites. In SEM micrographs cellulose fiber structures can be seen easly. They possess irregular shapes. Huntite hydromagnesite mineral particles of 10 micron size were seen in W60H sample. EDS analysis proved XRD and XRF result because C, O Mg, Al, Si and Ca elements were observed and there is any other element as impurities. It was found that by adding mineral particles denser composite structure was obtained.

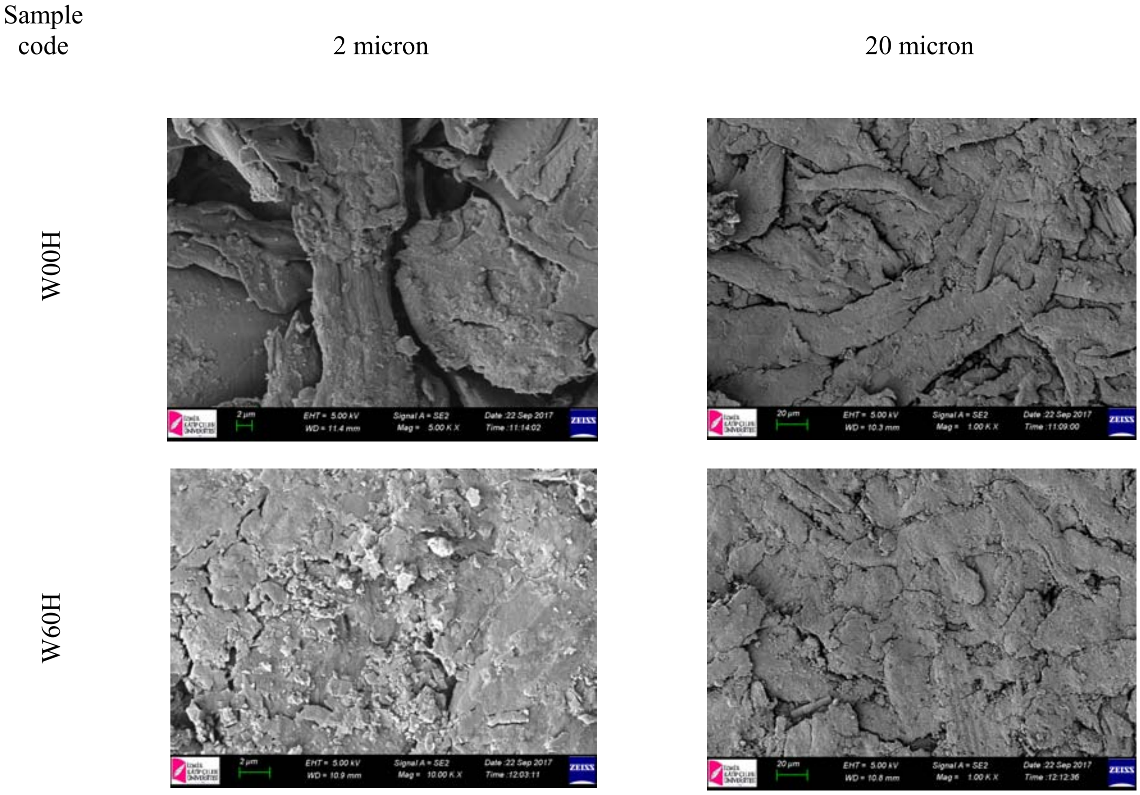
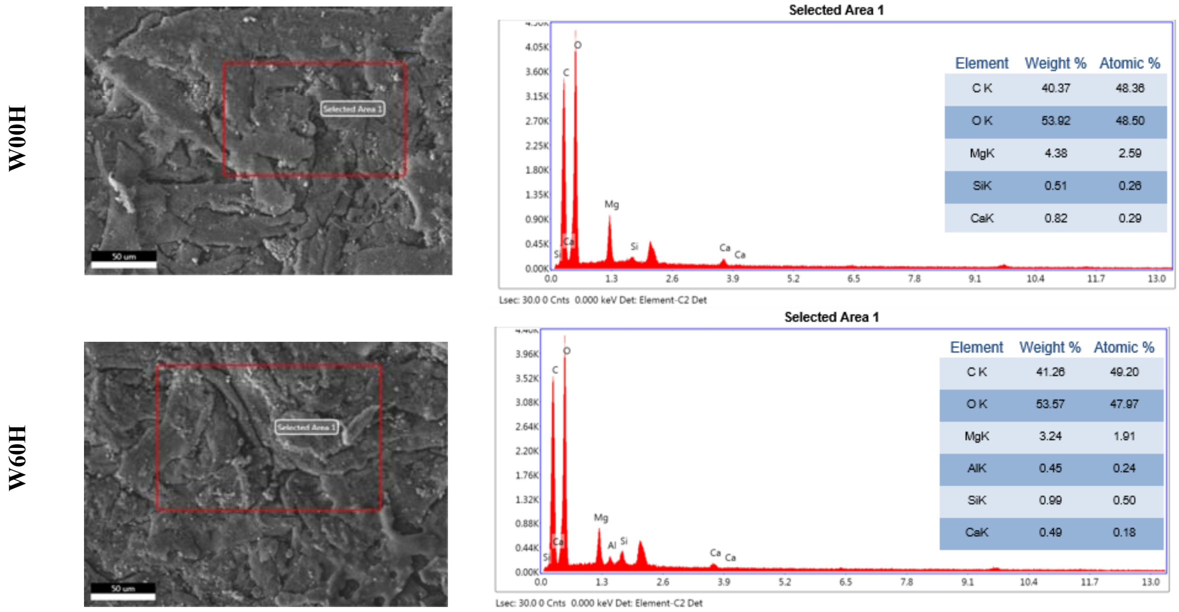


Figure 8. SEM analysis of samples of W00H and W60H



W00H:

Element	Weight %	Atomic %
C K	40.37	48.36
O K	53.92	48.50
MgK	4.38	2.59
SiK	0.51	0.26
CaK	0.82	0.29

W60H:

Element	Weight %	Atomic %
C K	41.26	49.20
O K	53.57	47.97
MgK	3.24	1.91
AlK	0.45	0.24
SiK	0.99	0.50
CaK	0.49	0.18

Figure 9. EDS analysis of samples of W00H and W60H

Table 2 depicts flame retardant test results. According to UL94 test, the results demonstrate the degree of flame retardant property of huntite hydromagnesite reinforced wood composite materials as a function of particle content. In between 0-45% content there was not indicated any flame retardant property, thus those samples can be defined as flammable. However, starting with 50% of mineral additive (W50H), the material became flame retardant as the flame was extinguished before 30 s according to the UL-94 standard. It can be easily seen that increasing the mineral filler amount improves the flame retardant property of the composite.

In our previous studies huntite and hydromagnesite minerals were investigated for the flame retardant property especially in polymeric composites; such as electrical cable applications, cable trays, window panels, polymeric flame retardant coatings etc (Yılmaz Atay & Çelik, 2013). In this study it is tested in wood composites and not surprisingly it was observed that the mineral was worked as flame retardant filler, too. The mechanism was similar as huntite hydromagnesite mineral undergoes an endothermic decomposition with water and carbon dioxide. By using this mineral in the wood materials, it will help to increase safety in virtually every wooden area of human existence. Therefore, this forgotten material in all kind of industries can get back its importance which it lost due to its flammable property.

Table 2. UL-94 test results of wood composite samples.

Sample Code	Flame applying time	Burning time	Result
W00H	10	30	Out of spec.
W20H	10	0	
	10	30	Out of spec.
W25H	10	30	Out of spec.
W30H	10	0	
	10	30	Out of spec.
W35H	10	30	Out of spec.
W40H	10	0	
	10	30	Out of spec.
W45H	10	30	Out of spec.
W50H	10sn	0sn	
	10sn	0sn	
	30sn	25sn	O.K.
W55H	10sn	0sn	

	10sn	0sn	
	30sn	24sn	O.K.
W60H	10sn	0sn	
	10sn	0sn	
	30sn	7sn	O.K.

Conclusion

Fighting fires depends on directly fire precautions and is directly related to the use of non-combustible material. Even if the fire started, flame retardants help to extinguish in the early stages of fire and prevent the dispersion of the flame. The flame retardant behavior of Turkish huntite hydromagnesite mineral in wood composite was investigated in this study. Wood composite was formed by using auxiliary mineral flame retardant additive introduced into the combustible product. It was found somewhat more effective by UL-94 flame retardant test. Thereby, it was depicted that by using the mineral reinforced wood composite, wood can get back its importance which it lost due to its flammable property. It was observed that increasing the loading amount of the additive increases the flame retardant property of the composite. For the further investigations mechanical behavior needs to be tested. Moreover, if different particle size of the minerals is used, it would be possible to obtain improved flame retardant properties. Therefore, to obtain the best performance, it is required to consider optimum mineral amount and the particle size. On the other hand, additive amount can be evaluated according to use conditions of wood composite; such as, where the composite will be used, what kind of load it will be applied, to what kind of environment it will be in, and so forth.

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