

# Investigations of Flame Retardant Properties of Beneficiated Huntite and Hydromagnesite Mineral Reinforced Polymer Composites

H. Yilmaz Atay

**Abstract**—Huntite and hydromagnesite minerals have been used as additive materials to achieve incombustible material due to their inflammability property. Those fire retardants materials can help to extinguish in the early stages of fire. Thus dispersion of the flame can be prevented even if the fire started. Huntite and hydromagnesite minerals are known to impart fire-proofing of the polymer composites. However, the additives used in the applications led to deterioration in the mechanical properties due to the usage of high amount of the powders in the composites. In this study, by enriching huntite and hydromagnesite, it was aimed to use purer minerals to reinforce the polymer composites. Thus, predictably, using purer mineral will lead to use lower amount of mineral powders. By this manner, the minerals free from impurities by various processes were added to the polymer matrix with different loading level and grades. Different types of samples were manufactured, and subsequently characterized by XRD, SEM-EDS, XRF and flame-retardant tests. Tensile strength and elongation at break values were determined according to loading levels and grades. Besides, a comparison on the properties of the polymer composites produced by using of minerals with and without impurities was performed. As a result of the work, it was concluded that it is required to use beneficiated minerals to provide better fire-proofing behaviors in the polymer composites.

**Keywords**—Huntite, hydromagnesite, flame retardant, mechanical property, polymeric composites.

## I. INTRODUCTION

FOR many years, minerals have been used in a wide variety of polymer applications. Moreover, they have been regarded as cost reducers and/or fillers. However, this is not necessarily the case today. Minerals are used for the properties and enhancements they bring to polymer applications. These application properties are closely related to the physical properties of the mineral itself [1], [2]. Thus, in the formulation of polymers, ancillary materials are added that impart to the compound the required properties of; flowability of the melt, tensile strength, bending strength, resistance to breakage by impact, resistance to the effects of oxygen or UV light, resistance to fire, suppression of smoke in the event of ultimate burning.

In the flame-retardant market, there are different types of products in use. The materials containing chlorine or bromine bonded to carbon are halogenated flame retardants. Whereas organo-phosphorous flame retardants contain phosphorous bonded to carbon. Those flame retardants are known for

causing some serious health problems, for instance disruption of hormones, developmental and reproductive problems. The chemicals in this kind of materials do not stay in products but they have been ascertained in the blood, fat and breast milk of nearly all people tested. Further, they can be shown up ubiquitously in wildlife and worldwide environment [3], [4]. Since those flame retardants have been legislated away because of mentioned health problems, mineral based flame retardants gain importance. These materials are inert substances can be added to flammable materials. By extension, stiffness, hardness, physical properties, optical properties, thermal properties, impact strength and flame resistance properties can be improved. Some of the mineral fillers are hydrated alumina, calcium carbonate, fly ash/mica hybrid, clay, huntite and hydromagnesite [5]. Generally, flame-retardant minerals consist of hydroxides (or hydrous carbonates) that endothermically decompose at temperatures between 200-400 °C. Produced water steam and carbon dioxide provide a cooling effect and this leads to quenching. Flame retardant materials are enhanced by the formation of a kind of ceramic layer being formed on the compound surface. This protects the ignitable materials from further attacks by flames and heat (Fig. 1) [6], [7].

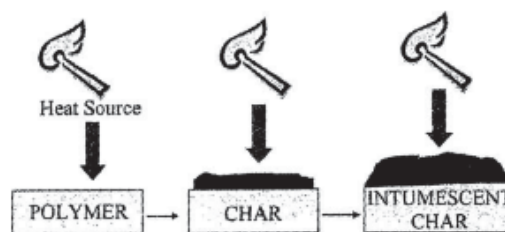


Fig. 1 Char and intumescence formation [8]

Here, in this work, huntite and hydromagnesite mineral is used in the polymer application for its flame retardancy properties. This mineral is one of the magnesium containing source for mineral flame retardants and it was introduced to the market in the late 1980s. At present, the commercially used deposits are located in Greece and Turkey. The deposit is a physical blend of two minerals huntite and hydromagnesite with varying ratios. The level of impurities is low, the most important ones are other white carbonate minerals such as aragonite, calcite, and dolomite. Endothermic decomposition starts at 250 °C. Water steam and carbon dioxide are liberated.

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This results in Ca and Mg oxide as solid end products (1) and (2) [9]:



In the previous works [10], physical characteristics (particle size, surface treatment etc.) of huntite hydromagnesite mineral have been studied [11]-[15]. In this study, it was aimed to use beneficiated huntite and hydromagnesite in the polymer composites. It was predicted that beneficiated mineral will provide better flame-retardant property. Beneficiation was performed by flotation process. After producing beneficiated powders, the polymer composites were prepared by adding those minerals to ethylene vinyl acetate copolymer (EVA). Huntite and hydromagnesite reinforced polymer composite samples were characterized by using size analyzer, differential thermal analysis-thermogravimetry (DTA-TG), X-ray diffraction (XRD), scanning electron microscopy-energy dispersive spectroscopy (SEM-EDS), X-ray fluorescence (XRF) and limiting oxygen index (LOI) test.

## II. MATERIALS AND METHODS

### A. Preprocessing

The material is received from Isparta region in Turkey. Mixed sample was drawn in each case for detail characterization and the enrichment process. The material was crushed, ground and sieved to be separated into different size. Used four fractions are following: ( $\mu\text{m}$ ):  $+212$  ( $x > 212$ ),  $-180+106$  ( $180 \geq x > 106$ ),  $-75+38$  ( $75 \geq x > 38$ ),  $-38$  ( $38 \geq x$ ). The sieves were weighed and stacked up, with the smallest one at the bottom and the largest one at the top. The powder was weighted down from the top screen through to a pan placed underneath the sieves to collect the particles. Sieving process was applied to 100 g samples. Because required quantity is 50 g for the flotation process, the sieving step was repeated until 50 g product is obtained for each fraction.

Regarding beneficiation process, flotation method was used. Flotation is a surface chemistry-based unit operation for separating finely divided solid materials from a mixture of valuable and nonvaluable particles dispersed in aqueous suspensions (Fig. 3). Denver type flotation machine with one litre capacity was used. Na-Oleate was used as a collector for the flotation of huntite and hydromagnesite. The samples were conditioned with required amount of reagents and determined time. Flotation tests were carried out at fixed pulp density. As well as the pulp density, pH and agitation intensity are controlling parameters during the process. After flotation process is completed, concentrates and tailings were separately collected. Then they were dried, weighed and analysed. Table I depicts the flotation experiment conditions [16], [17].

XRD studies were carried out for the identification of mineral phases present with an X-Ray Diffractometer Rigaku SmartLab. SEM micrographs and EDS analysis were taken

with JEOL JSM-7600F.

TABLE I  
OPTIMUM CONDITIONING PARAMETERS FOR FLOTATION

Parameter	Optimum value, property, type
pH	Natural
Powder size distribution	-38, -75+38, -180+75, -400+180
Collector	Na-Oleate, 2000 gr/t
Frother	MIBC, 30 gr/t
Na-Oleat, conditioning time	3 min
Conditioning time with frother	1 min

### B. Fabrication of Composite Materials

Huntite/hydromagnesite powders with different sizes were mechanically mixed with EVA copolymer to fabricate composite materials. Additive the ratio was 50%. After blending the EVA and additive thoroughly, the composite mixture is passed onto two roll mills to form compression molded plaques. In total 4 extruded tapes, which have different sizes of additives were produced at the end of this step.

## III. RESULTS AND DISCUSSIONS

XRD analysis of the received material is shown in Fig. 2. It is found from this result that the basic minerals are hydromagnesite ( $\text{Mg}(\text{CO}_3)_3 \cdot 3\text{H}_2\text{O}$ ) and huntite ( $\text{Mg}_3\text{Ca}(\text{CO}_3)_4$ ). Magnesite and dolomite exists as the main impurity in the ore. And other impurities are aragonite and calcite. The analysis result supports Kirschbaum's studies [6] that the impurities are magnesite, aragonite, and calcite phases in huntite and hydromagnesite ore.

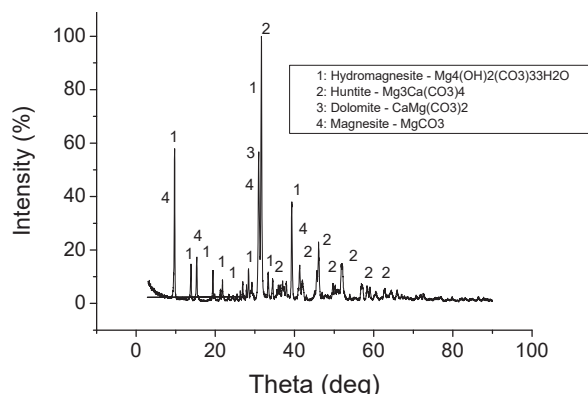


Fig. 2 XRD analysis of the material

Fig. 3 demonstrates SEM micrographs and EDS analysis of huntite and hydromagnesite mineral. It is clearly seen that mineral particles are not circular but they are lateral with irregular shapes. EDS analysis supports XRD result as Mg, Ca, C, and O were indicated. There seem no any other elements as impurities.

Flotation experiment results are demonstrated in Figure 4 and Table II. The beneficiation performance was evaluated according to the particle distribution. Very successful performance was achieved and it can be seen that decreasing

the particle size, increased the float quantity. That is to say that increasing the flotation performance. This may due to increasing of surface area and degree of liberation [18], [19]. Indeed, decreasing the huntite and hydromagnesite mineral particle sizes increased the float amount in the flotation process, i.e. using finer mineral particles improved the flotation performance.

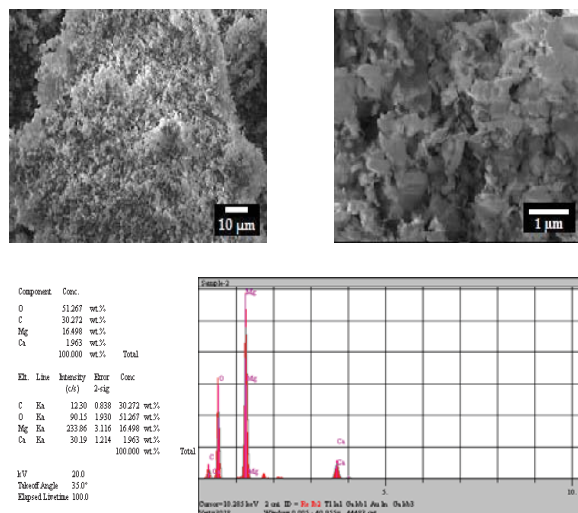


Fig. 3 SEM micrographs of huntite and hydromagnesite



Fig. 4 Flotation performance

On the other hand, this performance can be explained by a mechanism of the surface-collector interaction. It is related with the zeta potential differences on the surface of huntite hydromagnesite and its impurities [20], [21]. This experiment observed that the surface charges of huntite hydromagnesite are different than the impurities in the presence of Na-Oleat.

TABLE II  
HUNTITE AND HYDROMAGNESITE FLOTATION RESULTS

Size (µm)	Float (g)	Sink (g)	Recovery (%)
+212	13.87	36,13	27,74
-180+106	18.26	31,74	36,52
-75+38	19.68	30,32	39,36
-38	29.16	20,84	58,32

The quantitative phase analysis results are demonstrated in Table III. It can be seen that decreasing the particle size

increasing the huntite and hydromagnesite quantity in the float by supporting Table II.

TABLE III  
QUANTITATIVE PHASE ANALYSIS RESULTS OF FLOTATION PRODUCTS (FLOAT)

Size(µm)	Huntite + Hydromagnesite (g)	Magnesite and dolomite (gr)
+212	72,30	27,70
-180+106	84,10	15,90
-75+38	81,45	18,60
-38	84,30	15,70

With the analysis of XRF, MgO and CaO compounds were investigated for each flotation product. The results were illustrated in Fig. 5. It can be seen that CaO concentration is increased with decreased particle size. CaO refers to huntite due to its chemical formulation. Therefore, it depicts the increasing quantity of huntite in the flotation product.

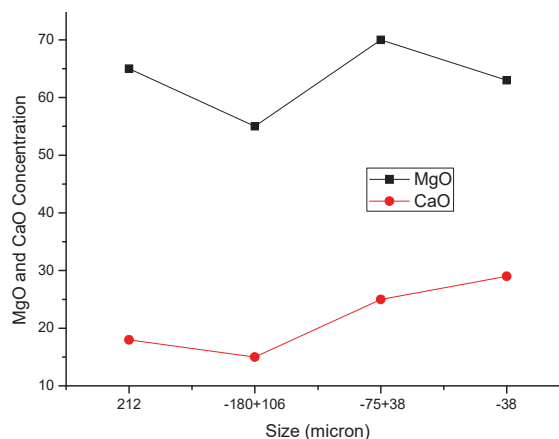


Fig. 5 MgO and CaO compounds distribution

Flame retardancy tests of the composites were performed. Oxygen index test measures the minimum concentration of oxygen in a flowing mixture of oxygen and nitrogen 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. This is called Loss of Ignition (LOI) value. According to the classification specifications lower than 24% is defined as flammable, 24-28% as limited flame retardant, 29-34% as flame retardant and above 34% is defined as excellent flame retardant.

In the present study the flame retardancy test results are shown in Fig. 6. It can be easily discerned that LOI values are increased by using finer particles flotation products. As it is mentioned above that depending on the flotation experiments, impurities were removed from huntite and hydromagnesite mineral and these purer minerals give better flame retardancy. In addition, this may be due to the increasing of surface area of the additives [10], [15].

On the other hand, in our previous work [22] it was observed that the mechanical properties and the flame

retardancy of the polymer composite were changed reversely regarding the mineral filler amount. In this study it is indicated that by using purer minerals the desired quantity of the additive minerals are reduced. Thus, the ratio of the deterioration of the mechanical property will be reduced.

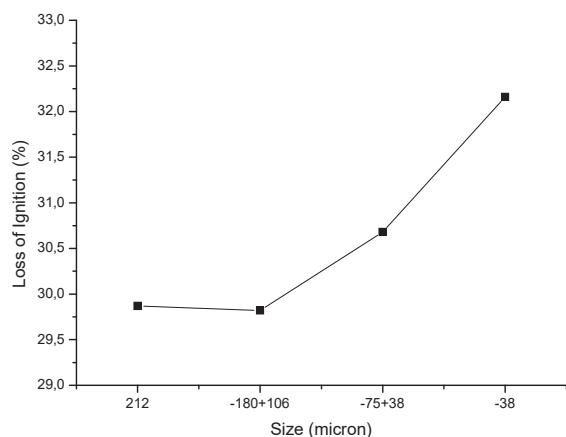


Fig. 6 LOI values of the specimens

#### IV. CONCLUSIONS

It was aimed to use purer minerals to reinforce the polymer composites. For this reason, huntite and hydromagnesite mineral was subjected to a beneficiation process. Regarding the flotation process, better performance was obtained by using finer particle size. This was observed by qualitative phase analysis and CaO concentration obtained by XRF. Decreasing particle size helps to get better flame-retardant behavior. By this way lower amount of mineral can be used to obtain similar flame-retardant degree. Therefore, it would be useful to keep the mechanical property of the composite. On the other hand, for improving flame retardant and mechanical properties of the composite, mixing is another important step to get well dispersion thus agglomeration should not be allowed in the composite.

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