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Size dependence of flame retardant composite coatings reinforced with huntite and hydromagnesite

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ABSTRACT

It has been highlighted the importance of huntite/hydromagnesite mineral as an innocent flame retardant material in the plastics in our previous works. In this study, flame retardant behaviors of huntite and hydromagnesite in the polymeric dye coatings were obtained and thesize dependence of this circumstance has been investigated. After getting different size of mineral powders, phase, microstructural and thermal analysis were undertaken using XRD, SEM-EDS and DTA-TG prior to the fabrication of the composite materials. The minerals with different particle size and content were subsequently added to the polymer matrix (epoxy dye) to produce composite materials. After the fabrication of composites, FTIR analysis has been done and the flame retardant behaviors were evaluated to determine flame retardancy of the coatings. It was concluded that by adding huntite/hydromagnesite mineral to the polymer matrix, flame retardant epoxy coatings were produced. And it was evident that decreasing the additive size is useful to achieve better flame retardancy.

KEYWORDS

Huntite/hydromagnesite;
Epoxy dye;
Coatings;
Polymeric composites;
Flame retardancy;
UL94;
Size distribution effect.

INTRODUCTION

In the point of the saving life, flame retardant materials play a significant role. Those materials act for delaying the spread of flame even if ignition occurs. So that they provide extra time in the early stages when the fire can be extinguished or an escape can be made. Hence flame retardant materials implement the most effective method for protecting life in combination with smoke detectors, fire alarms and related systems[1].

To obtain the flame retardant materials, ancillary flame retardants are added into flammable materials while converting the raw material into the finished product. Those materials put in to matrix to get demanded properties, such as flow ability of the melt, tensile strength, bending strength, resistance to breakage by impact, resistance to the effects of oxygen or UV light etc. along with resistance to fire or suppression of smoke in the event of ultimate burning[2].

The flame retardant materials are used either alone or in combination with other mineral flame retardants. A review of the applications can be classified as following;

- wire and cable applications such as wiring in telecommunication, under the hood automotive wiring, wiring in naval vessels, power stations and low smoke PVC cabling,
- construction industry applications, such as flooring, roofing tiles, conduits, profiles, coils, sheets, films to replace brominated flame retardants and PVC, partitions and paneling and insulating foams,
- electronic/electrical applications, such as relays, switches, plugs and sockets based on nylon, housing for electrical equipment, insulating and connecting parts and printed circuit boards[3].

An important example of the flammable materials is the polymers. They are highly combustible due to their chemical structure, which is made up mainly of carbon and hydrogen. The combustion reaction involves two factors: one or more combustibles, which are reducing agents, and a combustive, which is oxidizing agent. The combustive material is generally the oxygen in the air. The whole process usually starts with increasing the temperature of the polymeric material. This heating up induces polymer bond scissions. The volatile fraction of the resulting polymer fragments diffuses into the air and creates a combustible gaseous mixture. This gaseous mixture ignites when the auto-ignition temperature is reached, liberating heat. When the amount of heat liberated reaches a certain level, new decomposition reactions are induced in the solid phase, and therefore more combustibles are produced. The combustion cycle is thus maintained, and called a fire triangle as presented in Figure1[4].

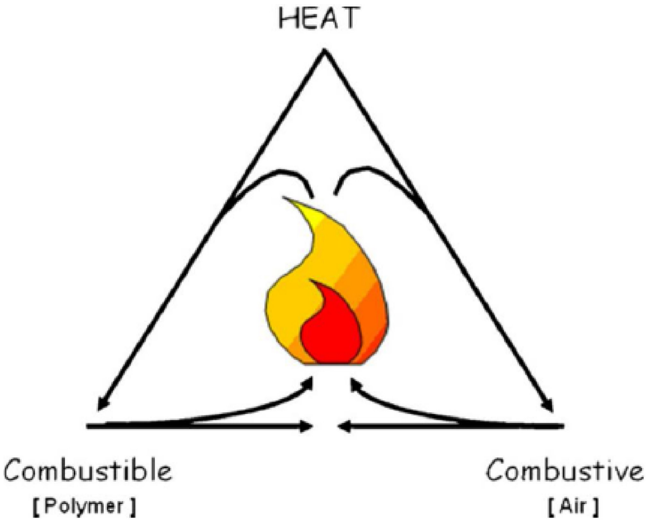


Figure 1 : Principle of the combustion cycle[4]

The thermal decomposition of a polymer is an endothermic phenomenon, which requires an input of energy. The energy provided to the system must be higher than the binding energy between the covalently linked atoms (200–400 kJ/mol for most C–C polymers). The decomposition mechanism is highly dependent on the weakest bonds, and also on the presence or absence of oxygen in the solid and gas phases[4].

To understand how flame retardants work, it is first necessary to see how materials burn. Solid materials do not burn directly, they must be first decomposed by heat (pyrolysis) to release flammable gases. Visible flames appear when these flammable gases burn with the oxygen (O_2) in the air. If solid materials do not break down into gases, then they will only smoulder slowly and often self-extinguish, particularly if they "char" and form a stable carbonaceous barrier which prevents access of the flame to the underlying material. For ingressing of oxygen to the fuel, this char serves as a barrier and also as a medium in which heat can be dissipated[1,5]. Flame retardant materials can act chemically and/or physically in the condensed phase or in the gas phase. In reality, combustion is a complex process occurring through simultaneous multiple paths that involve competing chemical reactions. Heat produces flammable gases from pyrolysis of the polymer and when the required ratio between these gases and oxygen is achieved, ignition and combustion of the polymer will take place (Figure 2)[5].

Flame retardant fillers have endothermic decomposition coupled with the release of inert gases. These two processes are generally found together, principally

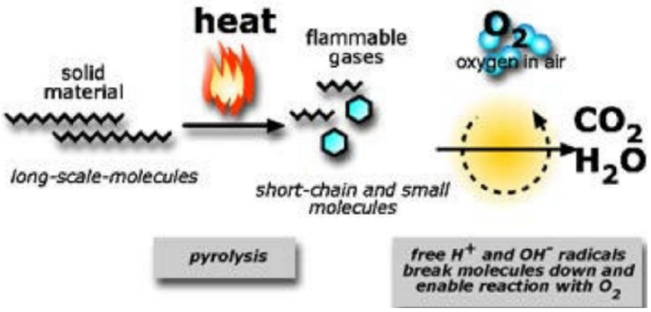


Figure 2 : Working mechanism of flame retardant materilas[1].

in some carbonates, hydrates and hydroxides[6]. Correspondingly, general flame retardant materials include hydroxides. Those 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 retardancy 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 as mentioned above[7,8].

Regarding the flame retardant materials used in the markets, generally, two main categories can be seen; 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[3]. Due to this, scientists have been studying to use of inorganic minerals as flame retardant additives. Aluminiumtrihydrate (ATO) and magnesium hydroxide are two main examples of those inorganic materials. In this study huntite/hydromagnesite mineral was used as magnesium hydroxide source of inorganic flame retardant. This mineral consists of physical blends of two minerals huntite and hydromagnesite with varying ratios in between 40-30% huntite and 60-70% hydromagnesite. 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/cm^3 and 2,24 g/cm^3, respectively[8,9].

Although, flame retardant materials remove a good deal of the heat evolved in the degradation and thus prevents further degradation, sometimes they cause the loss of mechanical properties due to being forced to be used at very high loadings[6,10]. Such that many fire retardants are used at very high loadings, which can significantly impact the physical properties of the polymer Nano composites become a part of an activity in this circumstance. The difference between the micro composite and the Nano composite is the dispersion of the material in the polymer. In a Nano composite, or the Nano-filler/additive, well dispersing throughout the matrix can be obtained. Nano composite formation may improvements in mechanical properties that usually occur through the formation of the Nano composite. Thus, same or better flame retardant property can be obtained by using shorter amount of additive in Nano scale[10,11].

Due to those reasons, it was experienced to use Nano scale minerals in this study. Huntite/hydromagnesite mineral has been crushed and ground to get finer fractions. At the end of the milling process different size of mineral powders were obtained. Then phase, microstructural and thermal analysis were undertaken using XRD, SEM-EDS and DTA-TG prior to the fabrication of the composite materials. The minerals with different particle size and content were subsequently added to the epoxy dye to produce composite materials. After the fabrication of composites, FTIR analysis has been done and the flame retardant behaviors were evaluated to determine flame retardancy of the coatings.

EXPERIMENTAL

Preprocessing

Huntite/hydromagnesite minerals($Mg_3Ca(CO_3)_4$/ $4MgCO_3.Mg(OH)_2.4H_2O$) were utilized in the epoxy coating/paints as flame retardant materials. First of all, the minerals were crushed and ground to 10 μm size. Then they were ground at room temperature for 0, 15, 30, 60 hours to Nano size particles in a High Energy Ball milling machine (Fritsch Premium line Pulverisette 7 model). The flame retardant powders were ground at the rate of 800 rpm at room temperature for 15 minutes in air.

Fabrication of coatings

Polymeric paint composite coatings were prepared by reinforcing flame retardant nanoparticles at different ratios into the epoxy matrix. Prior to the reinforcement of flame retardant nanoparticles, epoxy paint and its hardener were mixed with a 1:1 weight ratio respectively. After this procedure, different types of polymeric composites were prepared for flame retardant performance. Figure 3. Signifies a flow chart for production of flame retardant coatings.

The code of the ground huntite/hydromagnesite materials are listed in TABLE 1. The sample name was called according to grinding periods including 0, 15, 30 and 60 hours at room temperature in air. Then ground minerals were blended to the epoxy dye with different size and different loading levels. Afterwards, the plastic

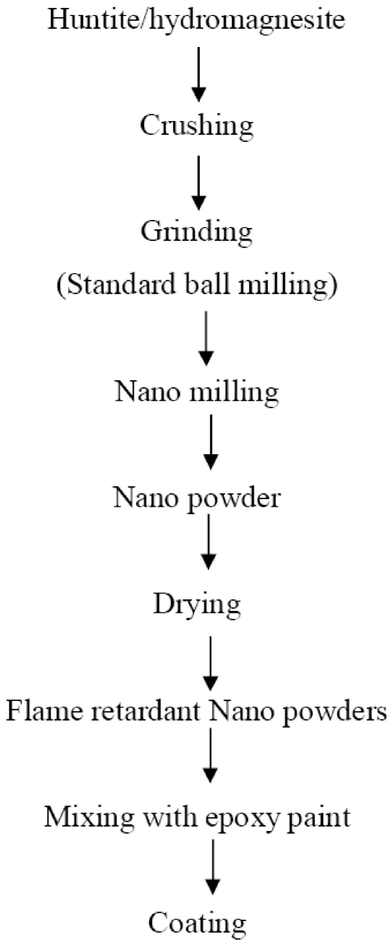


Figure 3 : Flow chart for production of flame retardant coatings

substrates are coated with those composite dyes. Coated samples and their descriptions are shown in TABLE 2.

Characterization

The thermal behaviors of hydromagnesite/huntite mineral, polymeric and composite material powders were evaluated to observe decomposition and phase formation at a heating rate of 10°C/min in the temperature range of 25-700 °C under air at-mosphere by using DTA/TG machine (DTG-60H Shimadzu). Al_2O_3 powder was used as a reference material. The enthalpies of solvent removal and combustion were obtained using TA 60WS software of Shimadzu 60AH. This software derived the enthalpies by calculation of total area under each peak with respect to the base line from start to end temperature. In order to determine thermal behavior of materials, DTA/TG (Shimadzu DTG-60H) analyses were performed under air.

TABLE 1 : The codes of the ground huntite/hydromagnesite materials

Sample names	Grinding periods
HM00	0 hour grinding
HM15	15 hours grinding
HM30	30 hours grinding
HM60	60 hours grinding

TABLE 2 : Sample codes and descriptions of flame retardant composite coatings

Sample code	Description
V00	Pure dye
VS 15-25	15 hours ground, % 25 huntite hydromagnesite added
VS 15-50	15 hours ground, % 50huntite hydromagnesite added
VS 15-65	15 hours ground, % 65huntite hydromagnesite added
VS 30-25	30 hours ground, % 25 huntite hydromagnesite added
VS 30-50	30 hours ground, % 50 huntite hydromagnesite added

FTIR (Perkin Elmer) absorption spectra of the composite materials were only measured over the range of 4000 to 400 cm^{-1} at room temperature. FTIR (Perkin Elmer Spectrum BX) spectra of composite materials were recorded to determine the organic components in the samples. After preparing powders at these temperatures, they were mixed with potassium bromide KBr. All of these five samples were characterized by FTIR by which % transmittance as a function of wavelength and % absorbance as a function of wavelength curves can be obtained.

The phase analysis of hydromagnesite/huntite minerals was performed by using a Rigaku D (Max-2200/PC Model XRD) X-ray diffractometer at 40 kV, 20 mA with a monochromatic CuK_{α} irradiation (wavelength, λ=0.15418 nm) by both θ-2θ mode and 2θ scan mode with a scan speed of 8 °/min.

The microstructural cross-sectional areas of huntite/hydromagnesite reinforced polymeric composite materials were examined by using a JEOL JJM 6060 SEM with an EDS attachment. Size factors and wettability properties of huntite/hydromagnesite minerals were examined in the composites using SEM-EDS. X-ray maps of Mg, Ca, C and O in the composites were evaluated.

Flame retardancy testing of the composites was performed. Generally, there exist two types of flame retardant tests including Limiting Oxygen Index (LOI) and UL94 for flame retardant tests. A LOI test machine 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[5]. UL94, this technique is used in plastic industry according to UL94 standardization. The material is conducted to the flame in a specific angle and distance. Extinguishing time of the flame and dripping ability are measured[12].

The UL94 test standard is a generally-used indicator of the acceptability of plastic for general use with regard to its flammability. There are three different tests; surface burn tests, vertical burn test, horizontal burn tests. Explanation of surface burn test used for our coated samples is below schematically in TABLE 3[13].

RESULT AND DISCUSSIONS

Powder characteristics

The flame retardant material is huntite/hydromagnesite powder, its powder characteristics were evaluated before coating process. The powders were characterized by DTA-TG, XRD and SEM-EDS.

Inasmuch as exothermic and endothermic reactions are significant in regard to flame retardancy properties, DTA-TG analysis are carried out to investigate the huntite/hydromagnesite minerals which were ground at different times such 0, 15, 30 and 60 hour(s). DTA-TG analyses are performed by heating up at the rate of 10 ºC/min at temperatures between 25ºC and 600ºC in air. DTA analysis of huntite/hydromagnesite mineral is demonstrated in Figure 4. Shows that there are three thermal reactions. Huntite and hydromagnesite have $Mg_3Ca(CO_3)_4$ and $Mg_4(OH)_2(CO_3)_3.3H_2O$ chemical formulas respectively. Note that 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 behavior 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 mix-

TABLE 3 : UL94 flammability ratings[13].

UL94 5VA	Burning must stop within 60 seconds after five applications of five seconds each of a flame to a test bar, and there must be no burn-through hole. The flame is larger than that used in Vertical Burn testing. This is the highest (most flame retardant) UL94 rating.
UL94 5VB	As for 94 5VA, but a burn-through hole is allowed.
a) Surface Burn tests	
UL94 V-0	Specimens must extinguish within 10 seconds after each flame application and a total combustion of less than 10 seconds after 10 flame applications. No samples are to drip flaming particles or have glowing combustion lasting beyond 30 seconds after the second flame test.
UL94 V-1	Specimens must extinguish within 30 seconds after each flame application and a total combustion of less than 250 seconds after 10 flame applications. No samples are to drip flaming particles or have glowing combustion lasting beyond 60 seconds after the second flame test.
UL94 V-2	Specimens must extinguish within 30 seconds after each flame application and a total combustion of less than 250 seconds after 10 flame applications. Samples may drip flame particles, burning briefly; and no specimen will have glowing combustion beyond 60 seconds after the second flame test.
UL94 VTM	Thin material version of the vertical burning test applied to thin or flexible materials which may distort, shrink or flex during the 94 V test. A specimen 200 × 50 mm is rolled longitudinally around a 12.7 mm diameter mandrel and taped on one end. When the mandrel is removed the specimen forms a cone shape, which gives it longitudinal rigidity. Have the same three classifications as 94 V. Differences are that a flame is applied twice for only three seconds, and no specimens may have flaming or glowing combustion beyond a point 125 mm from the bottom of the specimen.
b) Vertical Burn tests	
UL94 HB	Slow horizontal burning on a 3 mm thick specimen with a burning rate is less than 75 mm/min or stops burning before a mark 125 mm away from the point of flame application. HB rated materials are considered 'self-extinguishing'. This is the lowest (least flame retardant) UL94 rating
c) Horizontal Burn test	

ture of $Mg_4(OH)_2(CO_3)_3.3H_2O$ and $Mg_3Ca(CO_3)_4$. Finally the third thermal effect starts at 503.94°C and ends at 598.29°C. In this case, heat absorption is -1,43 J. MgO and CaO are formed by the end of this process. The similar results can be found in Ref.[7]. 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.

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

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

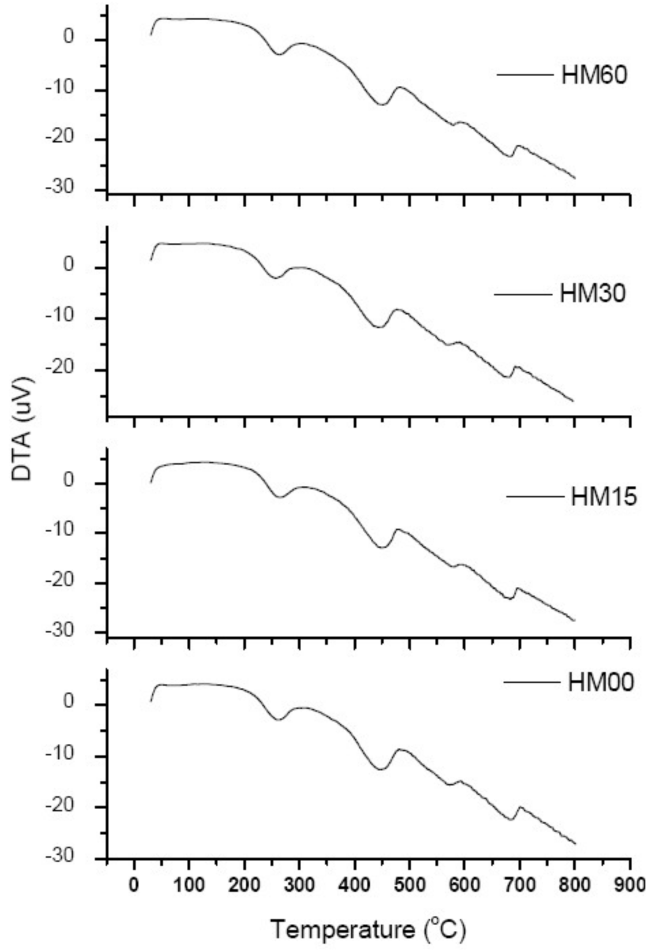


Figure 4 : DTA curves of groun huntite/hydromagnesite minerals.

As for TGA analysis, as depicted in Figure 5, the weight losses occur in huntite/hydromagnesite minerals as a function of temperature from room temperature to 800°C. It is indicated that the decomposition of huntite/hydromagnesite mineral occurs at temperatures between 400°C and 500°C. Total weight losses of huntite/hydromagnesite mineral were found to be 56 wt %. Rothon[14] indicated the decomposition temperatures of $Mg(OH)_2$ and $Al(OH)_3$ are 300-400°C and 250-350°C, respectively. Therefore it can be explained that huntite/hydromagnesite or even mineral reinforced composite sample have higher decomposition temperatures than $Mg(OH)_2$ and $Al(OH)_3$. The fact that decomposition temperature of huntite/hydromagnesite minerals is high and MgO and CaO ceramic materials are formed after burning process are quite likely to be a key area for development of flame retardant polymeric composite coatings. In the context of thermal properties of huntite/hydromagnesite minerals, it can be used as a flame retardant material.

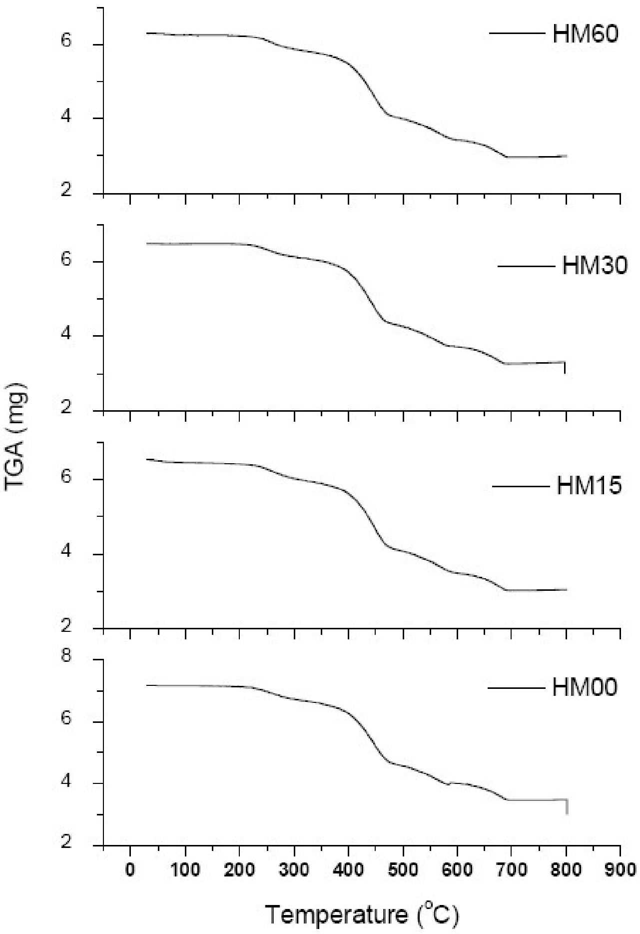


Figure 5 : TGA curves of ground huntite/hydromagnesite minerals.

The XRD pattern of huntite/hydromagnesite mineral powder is shown in Figure 6. It is found from this result that the basic minerals are hydromagnesite ($Mg_4(OH)_2(CO_3)_3.3H_2O$), huntite ($Mg_3Ca(CO_3)_4$) and dolomite ($CaMg(CO_3)_2$) in the raw huntite/hydromagnesite mineral. The most striking feature of the powder is that the main phases with high intensity are huntite and hydromagnesite. An average mineralogical composition, based on XRD and chemical analysis data of current ores is as follows huntite (46 %), hydromagnesite (46 %), magnetite (4 %), aragonite (3 %), and calcite (1 %). This finding in the current study is similar to Kirschbaum's research[9].

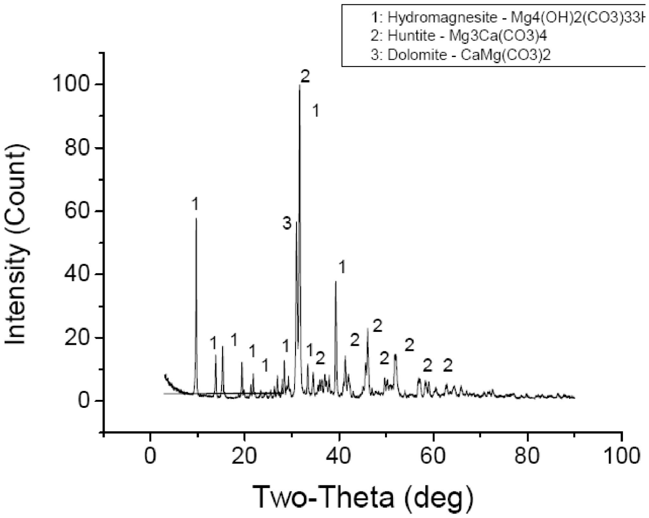
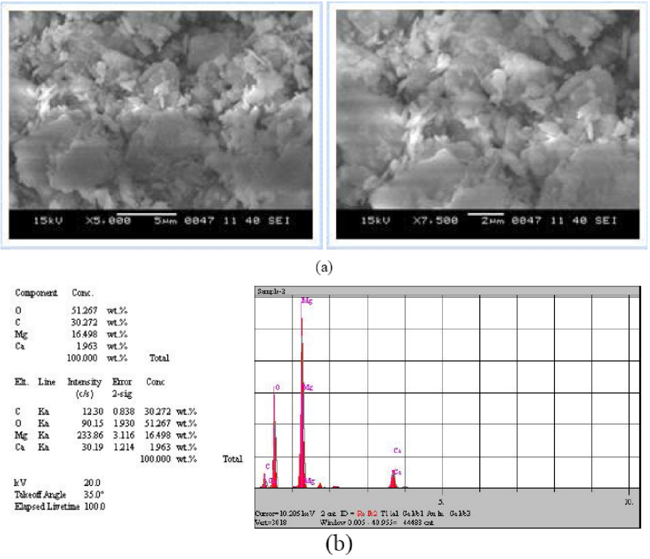


Figure 6 : XRD pattern of huntite/hydromagnesite mineral powder

Figure 7 demonstrates SEM micrographs and EDS analysis of huntite/hydromagnesite mineral particles. It is seen from Figure 8 that huntite/hydromagnesite mineral particles of 20 μm size possess irregular shapes after the grinding process. EDS analysis proved XRD result because Mg, Ca, C and O elements were found in the huntite and hydromagnesite mineral and there are some elements from ores as impurities.



(a)

Component	Conc.		
O	51.267	wt.%	
C	30.272	wt.%	
Mg	16.498	wt.%	
Ca	1.963	wt.%	
	100.000	wt.%	Total

Elt.	Line	Intensity (c/s)	Error 2-sig	Conc		
C	Ka	12.30	0.838	30.272	wt.%	
O	Ka	90.15	1.930	51.267	wt.%	
Mg	Ka	233.86	3.116	16.498	wt.%	
Ca	Ka	30.19	1.214	1.963	wt.%	
				100.000	wt.%	Total

kV	20.0
Takeoff Angle	35.0°
Elapsed Livetime	100.0

(b)

Figure 7 : SEM micrographs and EDS analysis of huntite/hydromagnesite mineral with 20 μm

SEM micrographs of ground huntite/hydromagnesite mineral powder samples at different magnifications such as 500X, 1000X, 2000X, 5000X and 10000X are denoted in Figure 8. The powders in Figure were ground at different times including 0, 15, 30 and 60 hours at room temperature in air. The grinding process of the minerals provides outstanding final flame retardant properties. While giving the anticipated benefits in grinding process of the powders, their mechanical and flame retardant properties are affected. When increasing grinding time from 0 hour to 60 hours, finer particles are obtained. These effects can be seen from SEM micrographs. Naturally, it can be stated that smaller the size of the mineral denser the composite coating/paint material. Note that this behavior increases the flame retardancy property of the material. As SEM micrographs are comparatively examined, the size of the powder ground at 0 hours is bigger than that at 60 hours.

Coating characteristics

Flame retardant reinforced composite coatings/paints were characterized after deposition process. Within the framework of the present study, experimental investigations were performed to characterize structural, microstructural and flame retardant properties of the composite/paints. Huntite/hydromagnesite reinforced composite coatings/paints were spastically characterized using FTIR and candle flame tester.

Figure 9 presents FTIR spectra of huntite/hydromagnesite mineral epoxy dye matrix composite coatings. The minerals used in the coatings were ground with different times containing 0, 15, 30 and 60 hour(s). Their effects were evaluated with this respect. It should be noted that there is no any influence of grinding process to organic bonding in order to form a new structure. In these experiments, the analysis was carried out in 500- 4000 cm^{-1} band range. It is important to realize that the high intensity band at 1500 cm^{-1} may related with C=C bonds in the matrix, and the weak bands at 600-700 cm^{-1} may related with C-H bonds. More specifically, those weak bands may be related with calcium carbonate bonds. The other interesting point is that there is no any interaction between huntite/hydromagnesite mineral and epoxy dye. Thanks to this reason, the composite coatings/paints were formed instead of a new polymeric material. In the composite

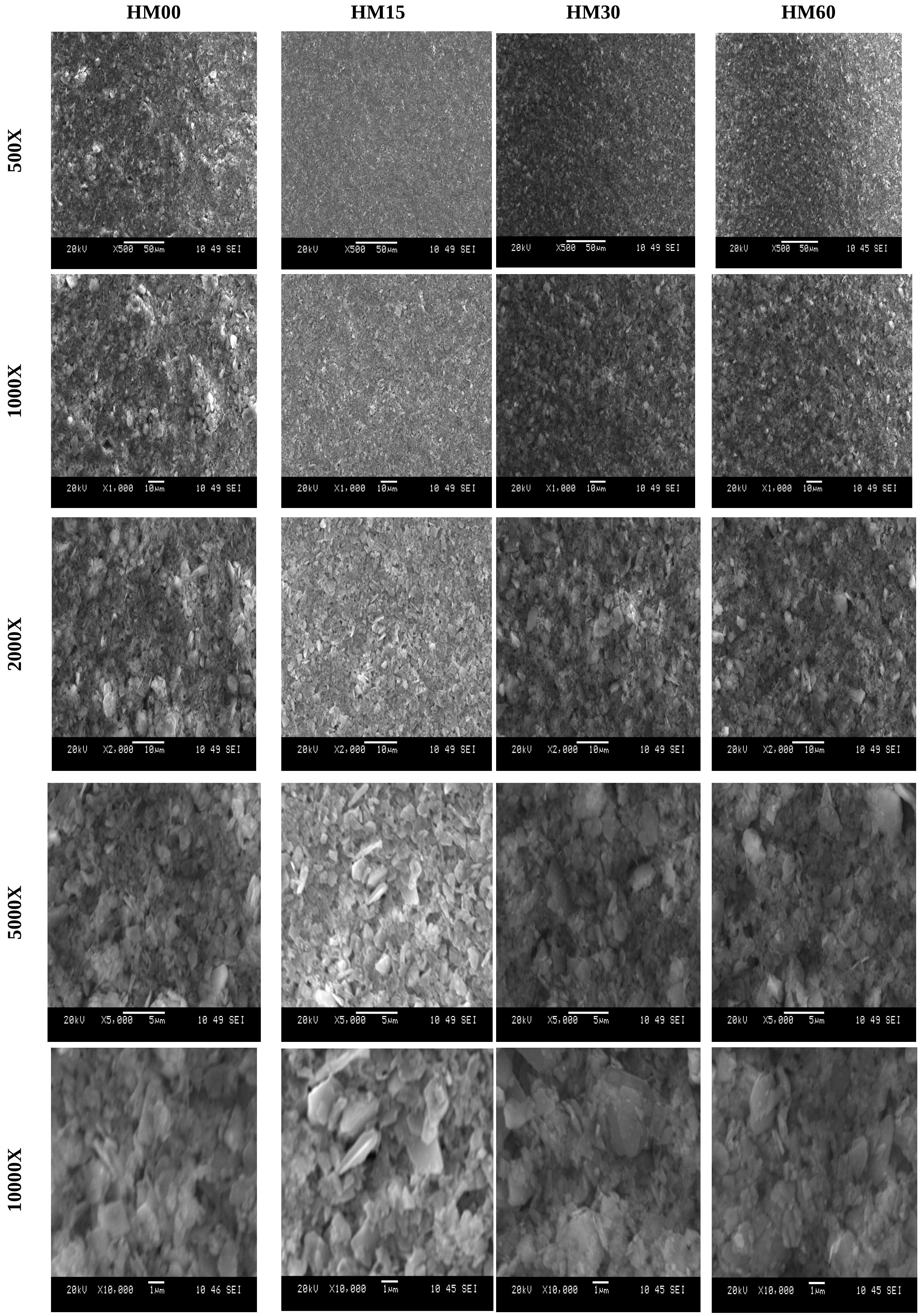


Figure 8 : SEM micrographs of ground huntite/hydromagnesite mineral powders at different magnifications

coatings/paints, structural modification did not alter in material chemistry. Only huntite/hydromagnesite mineral was embedded in the epoxy structure. In preparing composite materials with flame retardant content, it is necessary to achieve a homogeneous distribution of huntite/hydromagnesite mineral. To overcome this, the grinding process is a significant issue and consequently powder size of the mineral is an important factor. Even if there is any interaction between them, the powder with small size means homogenous mixture and strong mechanical strength and high flame retardancy in the composite coatings/paints.

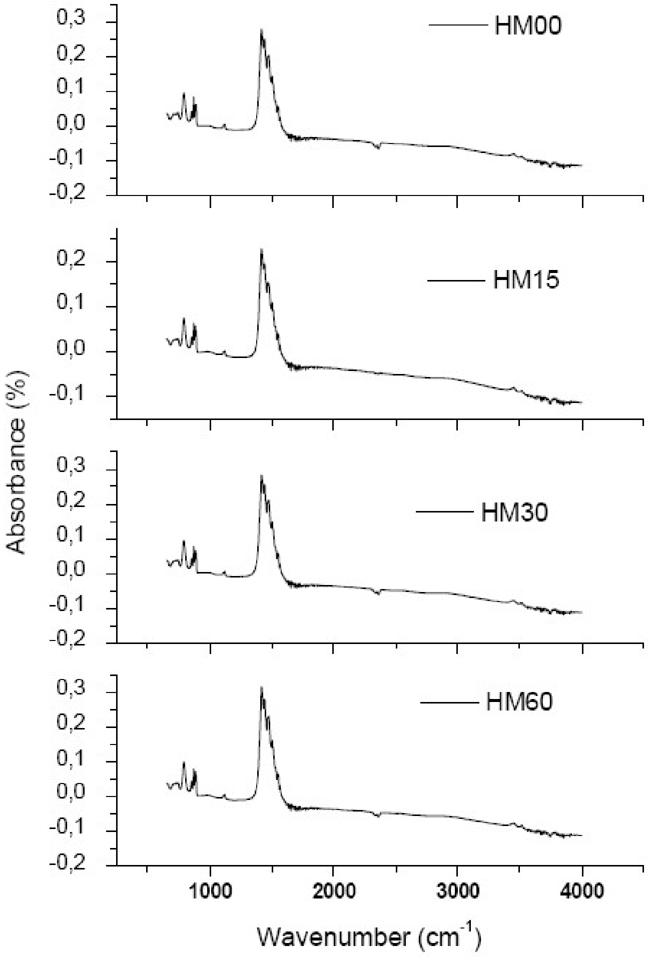


Figure 9 : FTIR spectra of ground huntite/hydromagnesite reinforced epoxy dye matrix composite coatings.

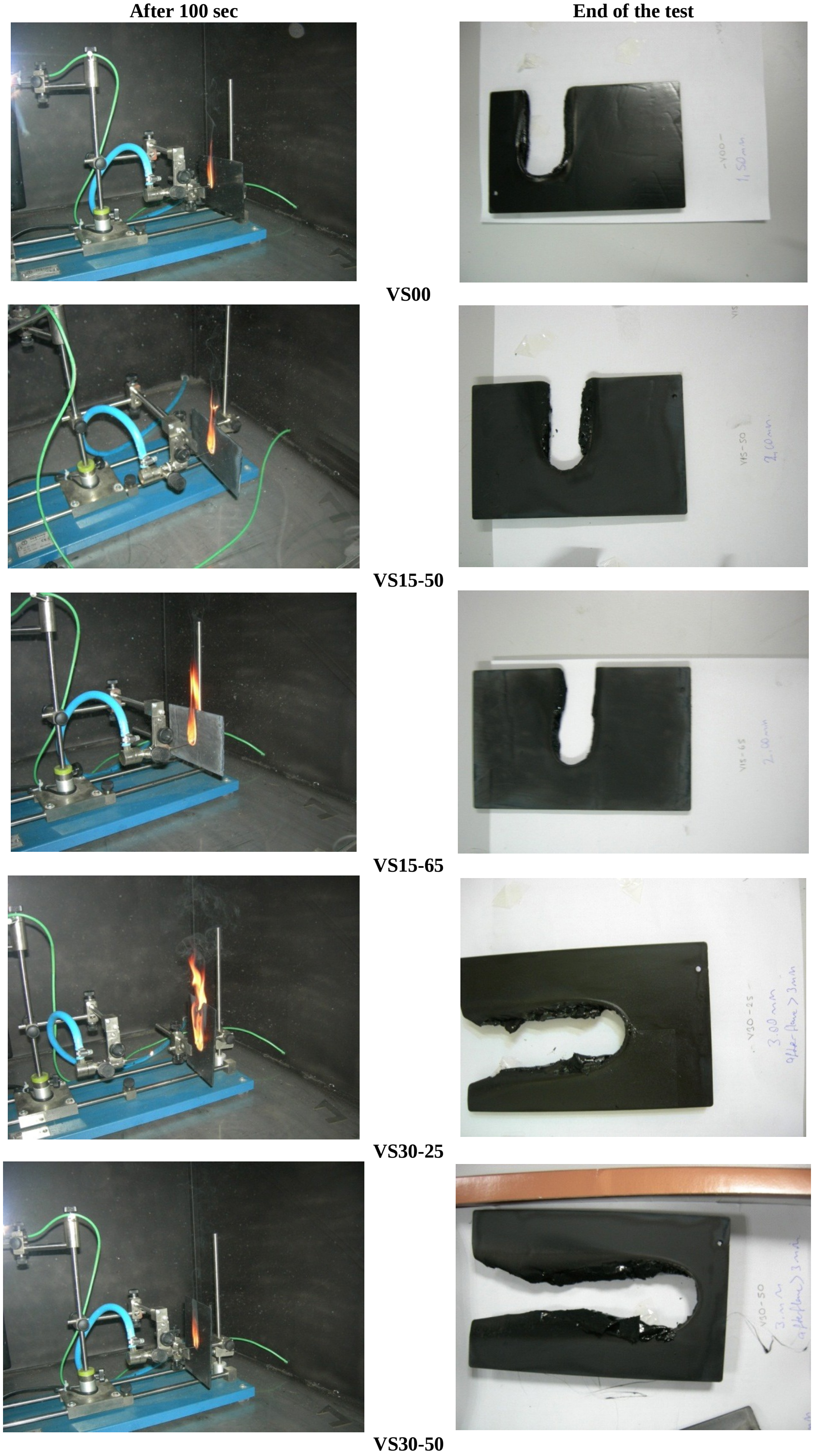
Huntite/hydromagnesite reinforced epoxy dye matrix composite coated plastic samples were subjected to flame retardancy tests as indicated beforehand, and the obtained results were presented in TABLE 4. The characteristic burning behaviors of huntite/hydromagnesite reinforced epoxy dye matrix composite coated samples including ground minerals are also shown in Figure 10.

TABLE 4 : Flame starting time of the samples

Sample name	Flamestarts	Afterflame	Results
V00	110 sec.	>180 sec.	NOK
VS 15-25	100 sec.	>180 sec.	NOK
VS 15-50	120 sec.	>180 sec.	NOK
VS 15-65	120 sec.	>180 sec.	NOK
VS 30-25	180 sec.	>180 sec.	OK
VS 30-50	180 sec.	>180 sec.	OK

Generally, it seems clearly that the composites with 30 hours-ground powder show better flame retardancy property than that with 15 hours-ground, this may be due to small particle size of huntite/hydromagnesite. So that comparing with the same grinding time and different loading level (VS1525 vs. VS1550 vs. VS1565 and VS3025 vs. VS3050); it can be seen that changing the loading quantity doesn't affect the flame retardancy so much, only flame starting time increased from 100 sec to 120 sec by increasing the loading level from %25 to %50 for the samples of VS1525 vs. VS1550. However, comparing with the same loading level and different grinding time (VS1525 vs. VS3025 and VS1550 vs. VS3050); it can be seen that changing the grinding time changed the flame retardancy behavior, such as increasing grinding time from 15 to 30 hr., the flame starting time increased from 100 sec to 180 sec for the samples of VS1525 vs. VS3025 and similarly, it is increased from 120 sec to 180 sec for the samples of VS1550 vs. VS3050. Therefore, it can be said that the main effective parameter is the particle size but not the loading level for the flame retardancy. So it is possible to obtain the same or better fire resistivity by decreasing the particle size and loading level. This result is similar our previous study performed with EVA polymers elsewhere[8].

Correspondingly, Ref[15] has been observed that different grades of the same fire retardant filler can give significantly different effects, despite apparent similarities in their endothermic decomposition or release of inert gas. Whilst this may, in part, be an outcome of the flammability test procedure applied, distinct particle size and particle morphology effects have been reported[10]. In parallel with our results, in relation to flammability,



After 100 sec

End of the test

VS00

VS15-50

VS15-65

VS30-25

VS30-50

Figure 10 : Burning behaviours of huntite/hydromagnesite reinforced epoxy dye matrix composite coated samples including ground minerals

Ref[15] shown that using the UL94 vertical burn test that the effectiveness of magnesium hydroxide in polypropylene increased with decreasing particle size. Similarly fine grades (<1 μm) gave markedly higher oxygen index values than coarser (45 μm) grades, particularly at filler loadings above 50% by weight, in studies involving PMMA modified with ATH.

Related with the mechanism of finer particles affectivity; it can be explained by that for instance in larger particles of ATH, water escaping nearer the center of the particle has a larger diffusion path, giving more time to react with alumina formed near the surface of the decomposing particle. During this process boehmite or psuedo-boehmite is formed and, being a partial decomposition product, is more stable than ATH, decomposing at about 450°C. In relation to the effects of particle size on thermal stability, decomposing time of the material increases. So this event delays the fire resistivity of the medium[15].

Depending on their nature and geometry, nanoparticles can contribute in various ways to improving the flame retardant performances of polymer materials. In this respect, a combination of the different types of nanoparticles can be expected to promote some synergetic flame retardant effects. Moreover, the combination of the nanomaterial can improve the cohesion of the residues recovered, which are much less cracked than those isolated separately from either Nano compositions[16].

On the other hand, although the samples of VS3025 and VS3050 passed the flame retardancy tests, they are just at the boundary of the standards. It can be said that the coatings are not good enough to get required flame retardancy property. This can be seen at Figure 11 that the middle parts of the mentioned samples are burned. This may due the thickness of the composite coatings. Conversely to our previous works, in this study dye polymers were used as a polymer matrix and the coatings were so thin films instead of massive plastics. So it is normal to not get the same good results with the previous plastics works. It can be said that to achieve better results, coating thickness can be increased, however at this time coating surface quality can become poorer. Or the grinding time can be extended to get finer particles. But this may be not economic for the industry application. Thereby, it needs to be estimated all the thickness, particle size and the cost together to meet the required fire retardant properties.

CONCLUSIONS

The flame retardant behavior of huntite/hydromagnesite minerals used as an additive in epoxy dye was investigated in this study. Huntite/hydromagnesite minerals were ground in a ball mill 0, 15, 30, 60 hours, they were blended into an epoxy dye and then glass and plastic substrates were coated with those composite dyes. At the end of the flame retardancy tests, it was found that 30 hours ground material had higher flame retardancy then 15 hours ground. It was concluded that decreasing the size of the additive increased the flame retardancy of the polymer composite, perhaps due to the fact that surface area of the additive was increased. Therefore it is clearly stated that decreasing average size of the mineral can help to achieve more flame retardancy in the polymer composite products.

Meanwhile, although two of samples passed the flame retardancy tests, the composite samples were not sufficient for ensuring adequate fire resistance to meet the required standards. This may due to inadequate coating thickness. To get better results and improving the flame retardancy of the dye coatings the coating thickness can be increased or particle size can be decreased. In addition, it can be accompanied by additional mechanisms in special systems or in combination with other flame retardants.

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REFERENCES

[1] Efra; Flame retardants integral to fire safety. Retrieved 15.08.2012 from http://www.cefic-efra.com/index.php?option=com_content &view =article&id=3&Itemid= 216&lang=en(2012)

[2] R.J.Mureinik; Flame Retardants, Minerals' growth in plastics.Euromin'97, Barcelona, IMIL Confer-

ence, 8-10 June **(1997)**.

[3] M.Weber; Mineral flame retardants, Overview & future trends. Euromin'99, European Minerals & Markets, Nice, IMIL Conference, 8-10 June **(1999)**.

[4] Laoutid, Bonnaud, Alexandre; Lopez-Cuesta & Dubois, **(2009)**.

[5] M.Xanthos; Functional Fillers for Plastic, NY: Wiley-VCH, **(2004)**.

[6] R.Rothon; Particulate-Filled Polymer Composites, Rapra Technology Limited, **(2003)**.

[7] R.Schmidt; In the line of fire, flame retardants overview, Industrial Minerals, 37-41 February **(1999)**.

[8] H.Yılmaz Atay, E.Çelik; Use of Huntite/Hydromagnesite Mineral in Plastic Materials as a Flame Retardant Polymer Composites, **31**, 1692–1700 **(2010)**.

[9] G.Kirschbaum; Minerals on fire, Flame retardants look to mineral solutions, 3rd Minerals in Compoundings Conference, IMIL-AMI joint conference, 8-10 April **(2001)**.

[10] H.Yılmaz Atay, Use of Huntite/Hydromagnesite Mineral in Plastic Materials as a Flame Retardant. Master Thesis, Dokuz Eylul University, **(2008)**.

[11] M.L.Bras, C.A.Wilkie, S.Bourbigot; Fire Retardancy of Polymers-New Applications of Mineral Fillers, Published by The Royal Society of Chemistry. Cambridge, UK, 4-6 **(2005)**.

[12] C.W.Leungand W.K.Chow; Review on four standard tests on flame sprading. International Journal on Engineering Performance-Based Fire Codes, **3(2)**, 67-86 **(2001)**.

[13] M.Tarr; Properties of laminates. Retrieved 04.08.2012 from http://www.mtarr.co.uk/courses/topics/0140_pl/index.html, **(2012)**.

[14] R.Rothon; Mineral Requirements for Flame Retardants, Industrial Minerals, December **(1994)**.

[15] Michel Le Bras, A.Charles Wilkie, Serge Bourbigot; Fire Retardancy of Polymers, New Applications of Mineral Fillers.Ch.2, The Royal Society of Chemistry, **(2005)**.

[16] F.Laoutid, L.Bonnaud, M.Alexandre, J.M.Lopez-Cuesta, P.Dubois; New prospects in flame retardant polymer materials From fundamentals to nanocomposites. Materials Scienceand Engineering R., **63**, 100–125 **(2009)**.