Nanoscaled $Mg(OH)_2$ Used as Flame Retardant Additive

Zhenhua Zhou, Zhihua Wu, Martin Fransson and Bing Zhou

Headwaters Technology Innovation, LLC
1501 New York Avenue, Lawrenceville, NJ 08648, zzhou@headwaters.com

ABSTRACT

Headwaters Technology Innovation (HTI) has applied aqueous colloidal chemistry with great success in the development of "bottom-up" nanomaterials and nanotechnologies. One such material is a nano-scaled magnesium hydroxide, NxCat® $Mg(OH)_2$, which is primarily used as a flame retardant additive. In order to maximize the water release and flame extinguishing effect, HTIG's manufacturing process allows for very small crystallites to form (~3 nm) and gives elaborately modified surface properties, leading to both a superior surface area and dispersion in the polymer/composite materials. With usage of NxCat® $Mg(OH)_2$, the plastic with 20% $Mg(OH)_2$ loading has better fire extinguish performance than that of conventional $Mg(OH)_2$.

Keywords: $Mg(OH)_2$, nanoparticles, flame retardant

1 INTRODUCTION

Various chemical compounds are used to retard ignition and burning in plastics. Supplied in powder, liquid or pellet form, flame retardants are incorporated into polymer formulations either as additives supplied to the polymer formulation during compounding or reacted into the polymer structure during polymerization [1]. The main flame retardants materials are halogens, phosphorus, inorganics and melamine compounds. Efforts are in place to ensure that the environment, health and safety issues for humans are sustained. In the past halogenated flame retardants were commonly used, but has been phased out by tighter restriction on the use of Green-house-gases. The use of halogen-free flame retardants is being adopted and a voluntary shift towards their use is also significantly increasing. The search for better and innovative flame retardant additives has resulted in a heterogeneous mix of compounds. New solutions to flammability are being offered by the $2.3 billion flame retardants market, which making up about 27% of the $8.6 billion 'performance' additives market [2].

Metal Hydroxides are well recognized alternatives to halogens. The most widely applied are aluminum hydroxide and magnesium hydroxide, the later being increasingly sought after in automobile and wire and cable applications. Magnesium hydroxide undergoes endothermic decomposition with water release at 630 ^{o}F (332 ^{o}C). The endothermic decomposition of $Mg(OH)_2$ which occurs during combustion is its flame retardant mechanism. For combustion to occur, there must be fuel, oxygen and heat. By absorbing some of the heat, magnesium hydroxide prevents or delays ignition and retards combustion of the polymeric material. The water released during decomposition has the effect of diluting the combustible gases and acting as a barrier, preventing oxygen from supporting the flame.

$$Mg(OH)_2 \rightarrow MgO + H_2O \quad 1316\ J/g \tag{1}$$

The smoke suppression properties of magnesium hydroxide are believed to be due to the dilution effect of the water vapor on the combustible gases or due to a char formation effect on the polymer.

However, up to 60% loading has to be used due to the low efficiency of the micro-size $Mg(OH)_2$, which impair the mechanical performance of plastic. In order to maximize the water release and flame extinguishing effect, HTIG's manufacturing process allows for very small crystallites to form (~3 nm) and gives elaborately modified surface properties, leading to both a superior surface area and dispersion in the polymer/composite materials.

2 EXPERIMENTS

2.1 Preparation

Headwaters Technology Innovation (HTI) proprietary technology has been applied to make nanoscaled magnesium hydroxide. The technology achieves great success in the development of "bottom-up" nanomaterials and nanotechnologies by using aqueous colloidal chemistry.

2.2 Characterization

Specimens were prepared for TEM analysis by dispersing the catalyst powder ultrasonically in isopropanol. A drop of the suspension was then applied onto a Cu grid covered with holy carbon and was dried in air. These samples were then examined by JEOL 2010F TEM/STEM operated at 80-200 KV.

Microscope: Microscope photographs were taken of each burn surface.

X-ray diffraction (XRD) measurements were carried out on a Philips PW1800 using Cu radiation at 40KV/30mA over the range of 20° to 70° with a step size of 0.05° and a counting time of 14 hours. Once the pattern was obtained, the phases were identified with the aid of the Powder Diffraction Files published by the International Centre for Diffraction Data.

2.3 Test

Samples were prepared by fluxing 80 grams of base resin on the Wright mixer. The flame retardant agent was added after flux of the base resin and fluxed into the molten polymer. The loading of flame retardant is maintained in 20 wt%. The mixture is placed in a compression mold and pressed. Observations were made with respect to dispersion, color and removal of the polymer from the mixer. The plaques were then subjected to horizontal burn testing to characterize differences in flammability.

3 RESULTS AND DISCUSSION

The TEM image indicates that the average particle size of nano-scaled magnesium hydroxide is ~3 nm, as showed in Figure 1. There is no apparent aggregation occurs in this sample. The nanoparticles are loosely bonded together to form a stable conglomeration. In Figure 2, the TEM lattice image indicates a Tweed microstructure due to a slight variation in crystal chemistry. It is possible that the material

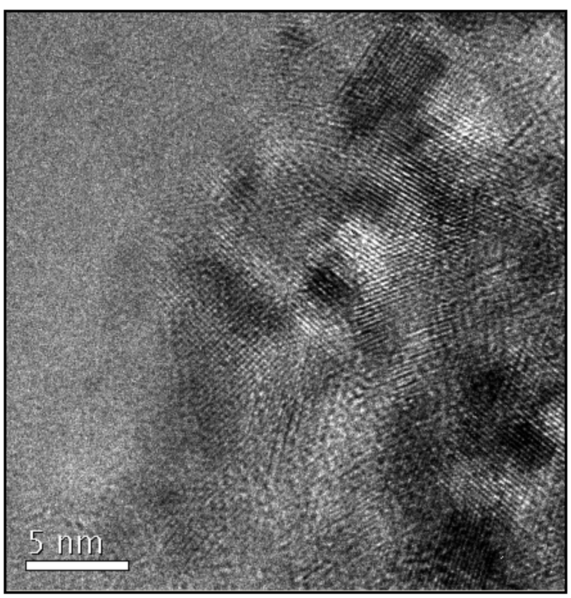


Figure 1: Transmission electron microscopy of NxCat® $Mg(OH)_2$

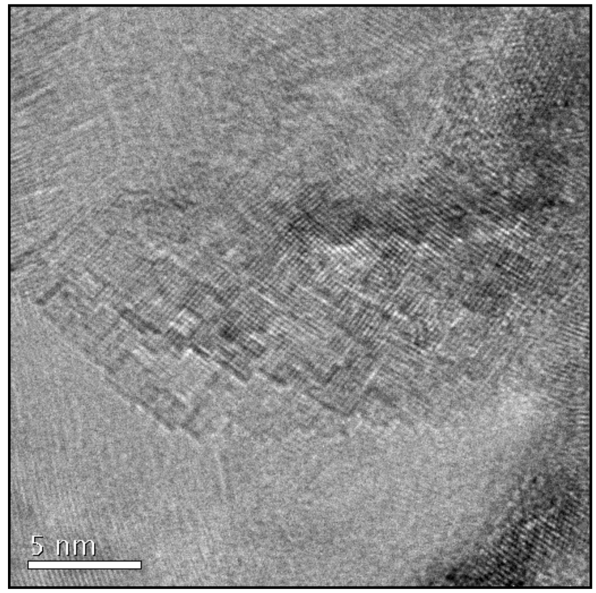


Figure 2: High resolution TEM micrograph showing Tweed microstructure

is slightly substoichiometric and is separating into the stoichiometric $Mg(OH)_2$ and hydrogen deficient MgO phases. These types of structures have been observed in simple binary oxides such as SnO and PbO. In these situations, the decomposition into two phases occurs over very short distances (10 Å to 100 Å) and the microstructure is often periodic. In addition, the decomposition seems to propagate in crystallographically soft directions so that the structure evolves on only 1-2 crystallographic planes. Thus, for X-ray analysis, one set of planes will appear to have the modulated structure (resulting in a very small particle size), while the other planes will not exhibit the modulations (resulting in a larger particle size). For the present sample, the 011 planes of $Mg(OH)_2$ exhibit a particle size of approximately 29Å, while the other planes exhibit a particle size of 117Å, as shown in figure 3. The MgO phase is more difficult to analyze since only one peak is observable and that gives an average size of 15Å. All of the remaining MgO peaks are obscured by overlap from the majority phase.

Two phases seem to be present in the diffraction pattern shown in Figure 3. The majority phase (~93%) is Mg(OH)2 (Brucite structure) as expected, but there is also a smaller quantity (~7%) of MgO (Periclase structure). The peak profiles are a bit unusual since some of the $Mg(OH)_2$ peaks are much broader than others. Typically, all of the peaks broaden in a similar way if the particle shape is uniform. But if the particle has a plate-like morphology, then some of the diffraction peaks will broaden more than others. Those peaks which represent planes parallel to the short dimension in the particle will broaden more, while those

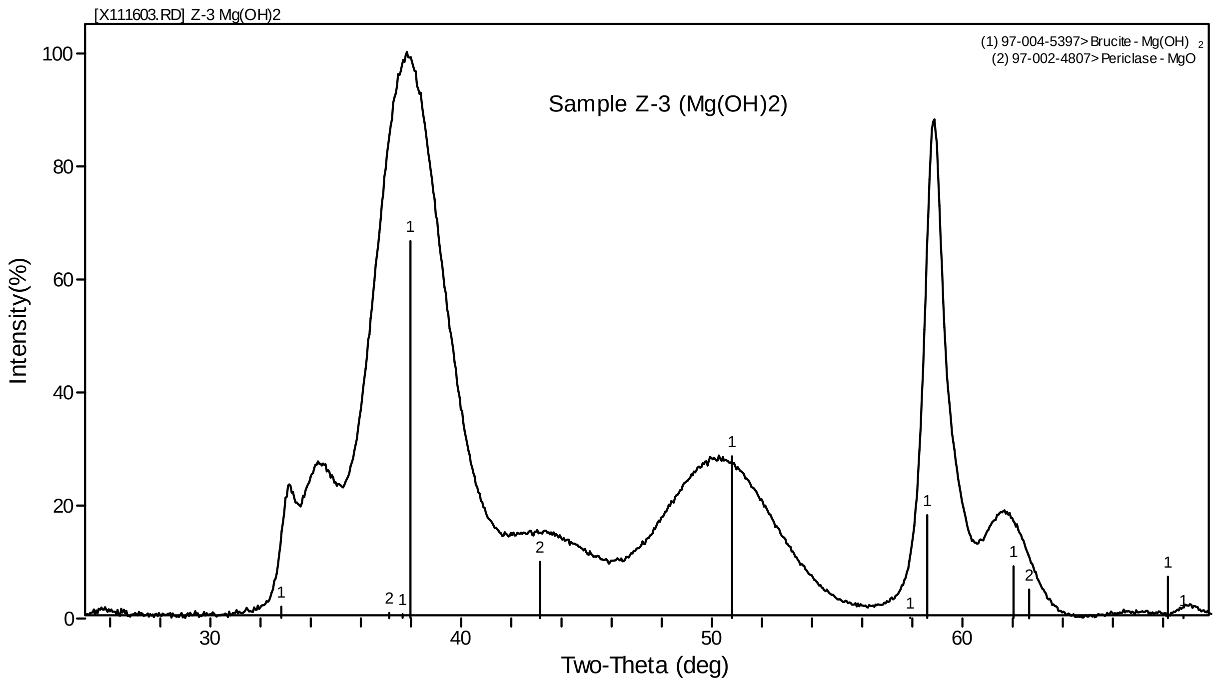


Figure 3: X-ray diffraction pattern for NxCat® $Mg(OH)_2$

planes perpendicular to the short dimension will result in diffraction peaks that broaden less.

The XRD results are consistent with the TEM images and indicate the presence of a Tweed microstructure. In such structures, the mottled structure usually lies in a single plane, which breaks up the structure into smaller domains. This is supported by the XRD results, which exhibit a small dimension for the 011 planes and a much larger dimension for the remaining planes. Thus, it appears that the material is hydrogen deficient and as a result, separates into two phases which differ in the hydrogen and oxygen concentration.

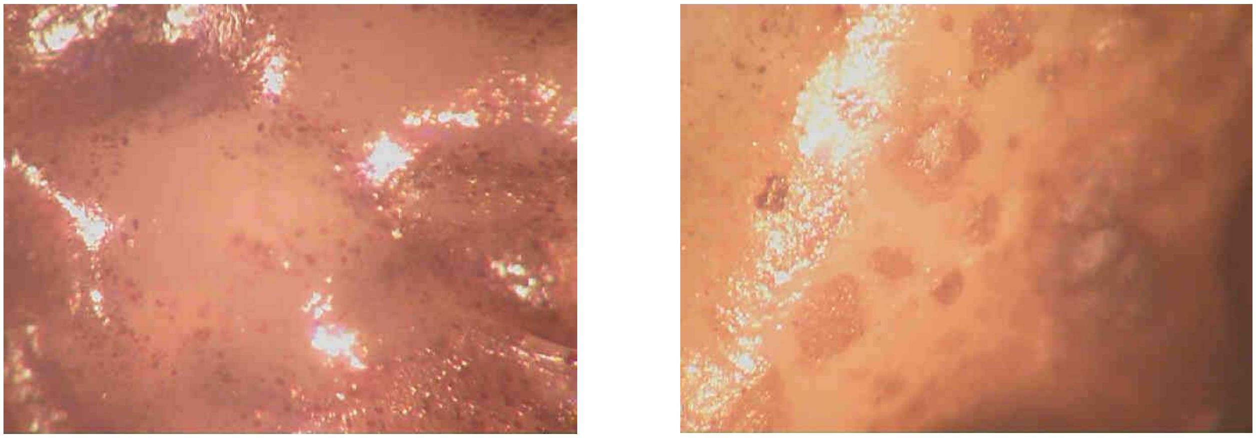
The horizontal burn testing has been used to characterize differences in flammability. The test results are showed in Table 1. Compared to conventional flame retardant, NxCat® $Mg(OH)_2$ give lower burn rate, i.e., 14 mm/min vs. 19.1 mm/min. It has been proven that flammability of flame retardant compounds is improved or optimized when the flame retardant agent particle size is small and the distribution of the flame retardant agent within the polymer matrix is very homogenous. From the previous TEM and XRD results, the smaller particle size has been observed for NxCat® $Mg(OH)_2$. Microscope photographs were taken of each burn surface after horizontal burn testing for further study of the flame retardant distribution in plastic. The distribution NxCat® $Mg(OH)_2$ in resin base at 20% is adequate and surface is glossy, as showed in Figure 4(a). Foaming present only in small localized domains. The surface of plastic with the conventional $Mg(OH)_2$ at 20% is glossy with large domains of $Mg(OH)_2$ with porosity in area surrounding these domains, as showed in Figure 4(b). The image of Figure 4(a) demonstrate better distribution and less aggregation with NxCat® $Mg(OH)_2$ compared to that of conventional $Mg(OH)_2$, showed in Figure 4(b). Apparently, both of smaller particle size and uniform distribution contribute the excellent fire extinguish performance.

For some flame applications, the plastic color has to be maintained as white or transparent. According to the observation, the NxCat® $Mg(OH)_2$ had acceptable white color after mixing, heating and pressing. All these features improve NxCat® $Mg(OH)_2$ application feasibility.

In conclusion, Headwaters Technology Innovation (HTI) proprietary technology can provide NxCat® $Mg(OH)_2$ with very small particle size (~ 3nm) and uniform distribution in plastic, which give improved performance of flame retardant.

Sample	**Burn Time (seconds)**	**Burn Length (mm)**	**Burn Rate (mm/min)**
Conventional $Mg(OH)_2$	235	75	19.1
NxCat® $Mg(OH)_2$	321	75	14.0

Table 1: horizontal burn testing to characterize differences in flammability.



. (a) (b)

Figure 4: Microscope photographs of $Mg(OH)_2$ filled plastic after burn testing

(a) NxCat® $Mg(OH)_2$; (b) Conventional $Mg(OH)_2$

REFERENCES

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