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# Clay-organic intumescent hybrid system for the synergetic flammability of polymer nanocomposites

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## Abstract

A polyethylene vinyl acetic acid (EVA) nanocomposite comprising of an intumescent agent that incorporates ammonium phosphate monobasic, mono-pentaerythritol, and melamine with a cationic nanoclay was set up through solution blending and melt blending to assess the fire retardancy utilizing a cone calorimeter. The results demonstrated that there was a significant reduction in the peak heat release rate of 70% contrasted with pure EVA. The fire retardancy of the clay-organic intumescent mixture framework composite was more successful than a same amount of additional nanoclay and intumescent agent. To check these outcomes, the residues of cone calorimeter samples were assessed alongside clay d-spacing changes amid utilization.

**Keywords** Electron microscopy · Nanocomposites · Thermal properties · X-ray techniques

## Introduction

Polymer materials are widely used in many types of construction, transportation, and electrical devices. However, basic polymer materials have been shown to have flammable properties. To overcome these drawbacks, many flame-retardant systems have been studied, including the representative aspects of these systems, such as nanometric materials (nanoclay, carbon nanotubes, graphene) and organic intumescent agent systems composed of acid sources and charring agents with a nitrogen gas source. Nanocarbon-based additives have shown good flame properties in composites [1–8]. However, these materials

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have drawbacks in terms of cost. For that reason, industrial organic intumescent additives and nanoclays are mainly used rather than nanometric carbon-based materials.

Usually, the traditional intumescent flame retardant is composed of three components: acid sources (phosphates, ammonium salts, etc.), carbonization agents (polyols, etc.), and blowing agents (melamine, etc.). The widely studied systems are used in industry and also show good flame retardancy and have an excellent char-forming ability [9]. During consumption, each component should demonstrate a chemical physical interaction with polymers and consumption of intermediate materials. Acid sources work for radical scavengers, carbonization agents provide a barrier effect in the condensed and gaseous phases, and blowing agents also provide shielding effects as well as a void and inert gas [10].

Nanoclay in a polymer composite has an effect on the decomposition of the polymer matrix. The active sites on layered silicates and acidic sites created by the decomposition of organoclay can catalyze the dehydrogenation, crosslinking, and charring of the nanocomposite. The protective coat-like char and physical–chemical crosslinking effect are responsible for the delay of thermal-oxidative degradation and decrease in the heat release rate (HRR) in the nanocomposite [7, 10].
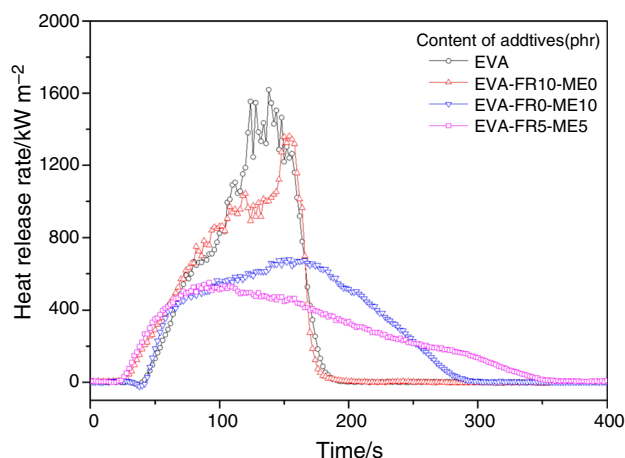
**Fig. 1** Heat release rate time-dependent curves for the cone calorimeter experiments: comparison of the efficiency of the same rate of additives for different compositions (i.e., frame retardants, nanoclays, retardant-clay)

Synergistic effects between the intumescent flame retardant and inorganic nanometric fillers (cationic clay, anionic clay, graphene, etc.) have attracted attention from both the industry and research fields [11]. The clay intumescent combined retardant system has beneficial aspects regarding material costs as well as retardant performance for industry. However, the clear reason for the synergetic effects was not defined [12–14].

Thus, in this study, we concentrated on the behavior of the nanoclay layer distance changes that occurred during the combustion process to test the synergetic flame retardancy mechanism by comparing composite samples of cone calorimeter test residue with original samples.

# Experimental

## Materials

For the matrix polymer ethylene vinyl acetate (EVA), VA420 was purchased from Lotte Chemical Corporation (Republic of Korea). Maleic anhydride grafted ethylene vinyl acetate (MA-g-EVA) was purchased from DuPont. SIME, the layered silicates (particle size below $\sim 1200$

nm), were purchased from Co-Op Chemicals. Cetyltrimethylammonium bromide was purchased from Sigma-Aldrich (Korea Ltd.). Toluene was used as a solvent. The flame retardant (FR) was composed of ammonium phosphate monobasic (APP), mono-pentaerythritol (PER), and melamine (MEL) (Sigma-Aldrich Ltd., Korea). For transmission electron microscope (TEM) sampling, Spurr resin, 3,4-epoxycyclohexylmethyl, poly (propylene glycol) diglycidyl ether, nonenyl succinic anhydride, and 2-dimethylaminoethanol were used (Ted Pella, Inc., Sweden) [15].

## Preparation of the nanocomposites

Pristine clays were mixed with deionized water at 80 °C, and cetyltrimethylammonium bromide was added to match the cation-exchange capacity of S1ME clay. The reaction mixtures underwent a 24-hour reaction. The final product was infiltrated, and the organoclays after vacuum drying were used after the product was dried for 24 h in a 100 °C oven. The organoclay was denoted as ME-CTA. Then, EVA was added to toluene. The dispersion of ME-CTA in the same solvent was added to the EVA solution and then continuously stirred for 24 h. The entire solution was evaporated in an oven at 100 °C for 12 h. White clay pre-dispersed EVA and the intumescent agent were mixed with weight 5% MA-g-EVA and passed through a twin screw extruder (BA-19, Bau-Technology, Republic of Korea). The composite contained ME-CTA 10 phr (part per hundred resin), intumescent agent (APP, PER, MER, 3:1:1 ratio) 10 phr, ME-CTA clay 5 phr, and intumescent agent (APP, PER, MER, 3:1:1 ratio) 5 phr, which were denoted as EVA-ME10, EVA-FR10, and EVA-ME5-FR5, respectively.

## Characterization and measurement

X-ray diffraction analysis of the nanocomposite samples and char residue was measured using a Bruker X-ray diffractometer (equipped with a 2-D detector) in reflection mode. Cone calorimeter (Fire Testing Technology Ltd., UK) tests (ISO 5660-1) was performed on compression-molded samples ($100 \times 100 \times 4$ mm$^3$) by placing the

**Table 1** Cone calorimetry data for pure EVA and its polymer compositions at an incident heat flux of 50 kW m$^{-2}$

| Samples | PHRR/kW m$^{-2}$ | THR/MJ m$^{-2}$ | ASEA/m$^2$ kg$^{-1}$ | AMLR/g s$^{-1}$ |
|---|---|---|---|---|
| EVA | 1619 | 111 | 387 | 0.123 |
| EVA-FR10 | 1362 | 105 | 739 | 0.103 |
| EVA-ME10 | 680 | 107 | 573 | 0.097 |
| EVA-ME5-FR5 | 550 | 98 | 551 | 0.076 |

*PHRR* peak heat release rate, *THR* total heat release rate, *ASEA* average specific extinction area, *AMLR* average specific extinction area, *AMLR* average mass loss rate
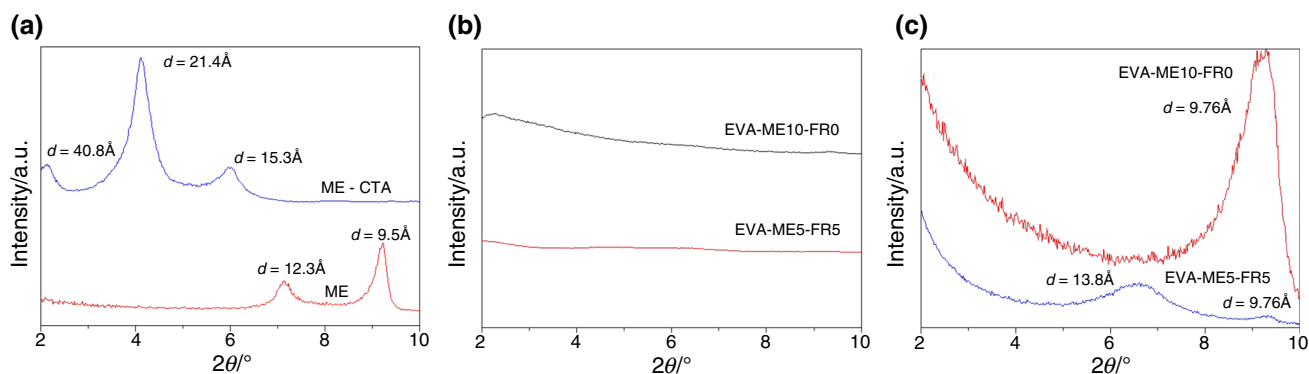
Fig. 2 X-ray diffraction spectrums, **a** S1ME host clay and organized clay using cetyltrimethylammonium bromide, **b** EVA-ME10 and EVA-ME5-FR10, **c** char residue of clay composite after cone calorimeter experiments
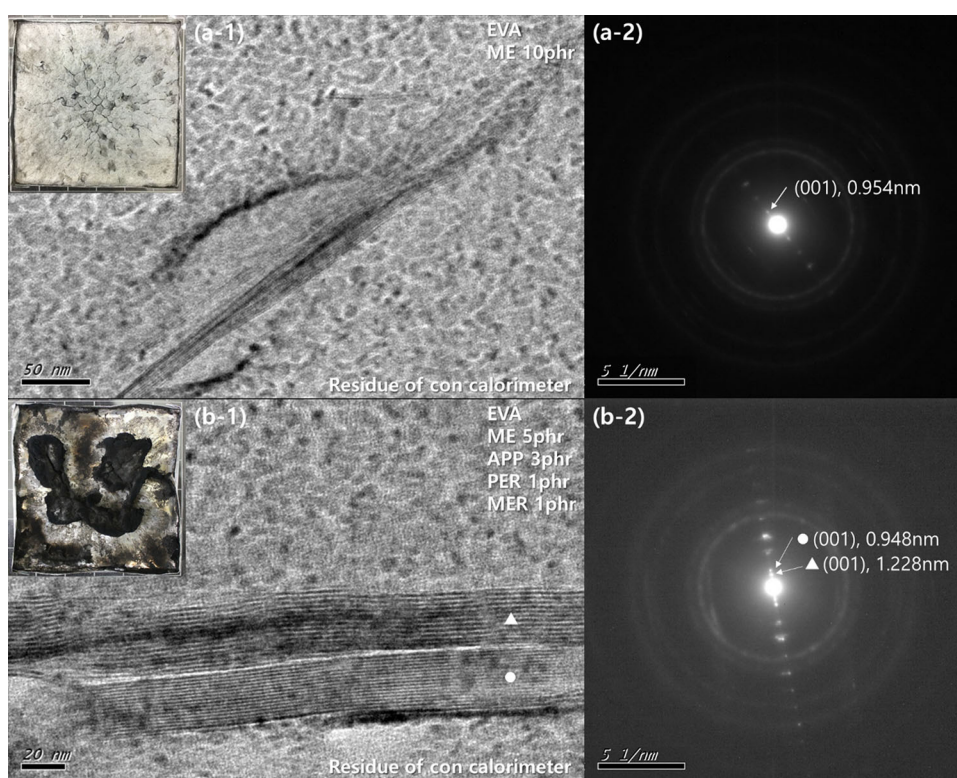


Fig. 3 **a-1** TEM image of the char residue of EVA-ME10. The inside image is an image of EVA-ME10 after the cone calorimeter test, **a-2** X-ray diffraction pattern of EVA-ME10, **b-1** TEM image of the char residue of EVA-ME5-FR5. The inside image is an image of EVA-ME5-FR5 after the cone calorimeter test, **b-2** X-ray diffraction pattern of EVA-ME5-FR5

samples horizontally with a flux of 50 kW m$^{-2}$. The nanocomposite samples and char residue ware examined by TEM (JEM-2100F, JEOL Ltd., Japan). For TEM sampling, the char residue was impregnated and fixed by Spurr resin [14], and then, frozen sections were sliced using a cryo-ultramicrotome (PT-PC Power Tome Ultramicrotome, Boeckeler Instruments, Inc.) before being coated with platinum.

# Results and discussion

The experimental results of the cone calorimeter tests for EVA and EVA-based composites, including EVA-ME10, EVA-FR10, and EVA-ME5-FR5, are shown in Fig. 1 and Table 1. EVA was very flammable and had a peak heat release rate (PHRR) that reached 1619 kW m$^{-2}$. By contrast, the intumescent agent dispersed composite showed
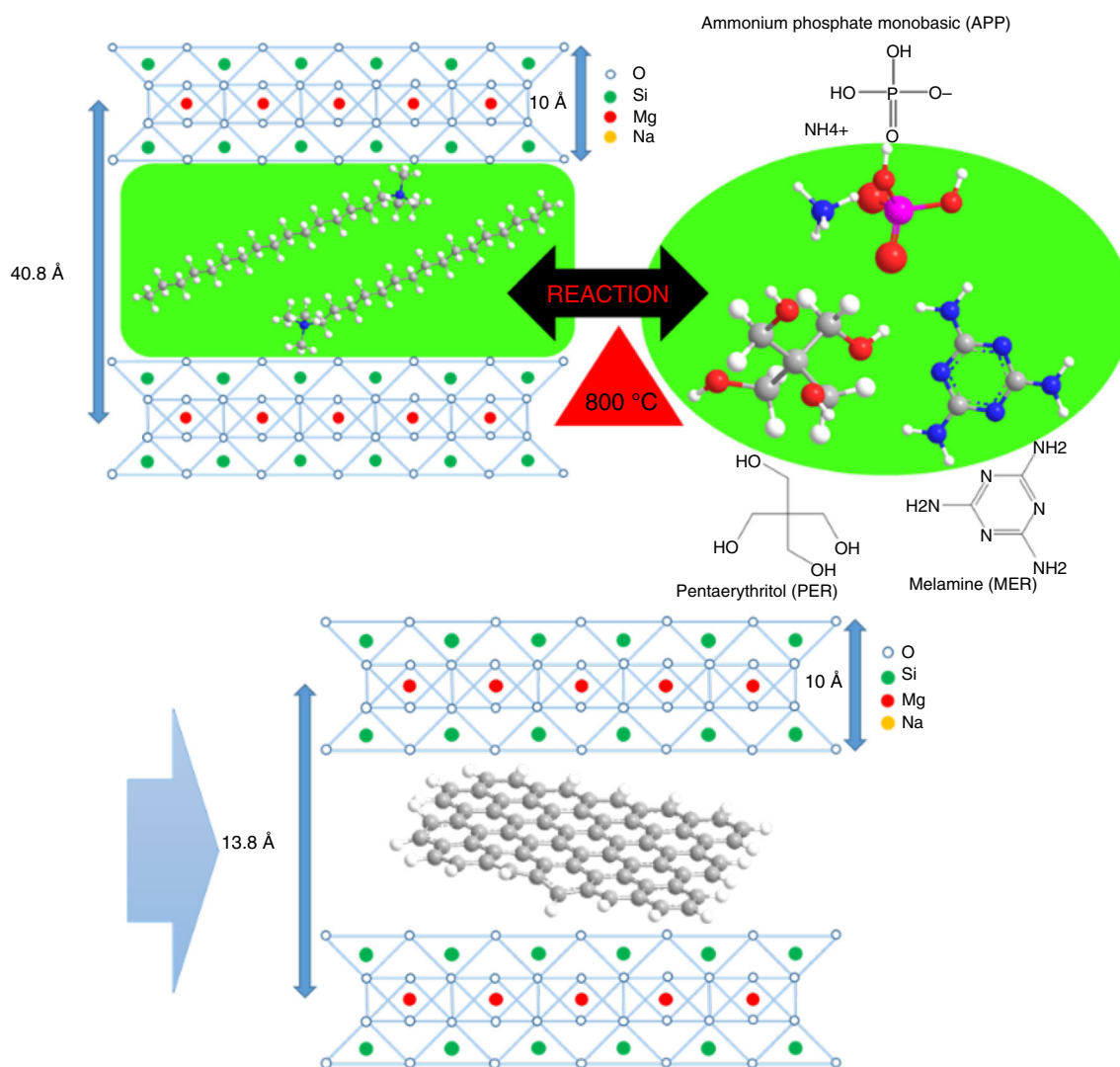
**Fig. 4** Schematic diagram of clay silicate layer distance changes through a clay intumescent reaction while passing through the cone calorimeter pyrolysis system

slightly better flame retardancy compared to EVA. Compared to pure EVA, the PHRR (1362 kW m$^{-2}$) of EVA-FR10 was reduced by 16%. ME-CTA as a nanometric filler showed better flammability than FR for the EVA composite. The PHRR (680 kW m$^{-2}$) of EVA-ME10 was reduced by 58% relative to pure EVA. The EVA-ME5-FR5 hybrid system had a synergetic flame retardancy property. The PHRR (546 kW m$^{-2}$) was reduced by 66% relative to pure EVA. Also total heat release rate (THR) and average mass loss rate (AMLR) displayed decreasing tendency. Exceptionally average specific extinction area (AMLR) show decreased, when intumescent agent and clay were added. These results exceeded those of EVA-FR5 and EVA-ME5 with addition of the same content. Each char residue mass showed a different morphology depending on the type of additives used, such as the millimeter scale of the char particle for EVA-ME10, which led EVA-ME10 to

have a wispy and feeble structure compared to EVA-FR5-ME5, which had an aggregated tight massive char structure (Fig. 3).

To explain the synergetic flammability of EVA-FR5-ME5, the nanoclay D-spacing changes were evaluated via XRD and TEM. The XRD spectra (Fig. 2) are shown, and untreated clay had 9.5 and 12.3 Å layer distances. The organification interlayer distances increased to 15.3 and 21.4 and 40.8 Å. The difference between the distances of these organoclays is due to differences caused by the structure of the surfactant [16]. ME-CTA was dispersed in EVA through a pre-solution and melt blending process, even though blending occurred with FR, as shown in Fig. 2b. Each char residue (EVA-ME10, EVA-FR5-ME5) of the cone calorimeter showed different D-spacing changes depending on the presence of FR. For EVA-ME10, char residue showed a strong single peak at approximately

9.76 Å. However, the EVA-FR5-ME5 char residue showed two signal peaks at approximately 9.76 and 13.8 Å, and this phenomenon occurred while the cetyltrimethylammonium surfactant was present between the layers of clay. APP was added as an intumescent agent and acted as an electronic withdrawing inhibiter, which interrupts the breakdown of the cetyltrimethylammonium and encourages the formation of a single carbon layer between the silicate layers [17].

For a more definite explanation of the synergetic flammability, the nanosilicate distant changes in char residue from the cone calorimeter were examined through morphological observations with TEM. The TEM observations are shown in Fig. 3. For the EVA-ME10 char residue, after evaluating the TEM X-ray diffraction (001) peak pattern, the silicate space distance shrank to 9.5 Å, similar to the host clay distance level, which evaluated the combustion process via the cone calorimeter test. A similar outcome was confirmed for the EVA-FR5-ME5 char residue sample. The TEM image showed that the two silicate layers had different layer distances after measuring the distances of the diffraction (001) peak pattern, which showed a single-layer distance of 9.48 Å and another distance of 12.28 Å in the same image. These results correlate with the XRD data and can be considered to be evidence for restacking, and different distances could be presented together.

Overall, the experimental outcomes were analogous to a consummation process. When the intumescent agent and organoclay were used individually and exclusively as flame retardants, the composite flammability had a low efficiency. However, in the intumescent-clay hybrid system, when the flame retardant properties arose from a polymer composite, there was synergetic flammability. This phenomenon can be explained through conjugation with clay restacking and the char generation process. Macroscale observations of the EVA-FR5-ME5 residue sample confirmed aggregation of the char residue and char that had a clay structure. EVA-ME5 had a wispy and dusty clay structure. The intumescent agent is considered to be related when pyrolysis occurs and the clay restacks. Therefore, the carbon layer is generated at the involved clay interlayer during thermal decomposition, as shown in Fig. 4. Therefore, EVA-FR5-ME5 can form a compact and dense clay–char layer compared to the other samples (EVA-ME10, EVA-FR10).

## Conclusions

This study investigated the effect of clay-organic intumescent hybrid system for the synergetic flammability of polymer nanocomposites. XRD and TEM were used to examine the distance space of each sample's silicate layer, before and after going through the cone calorimeter. The XRD result shows that the nanoclay was well modified with organic surfactants and thus organoclay was well dispersed in composite and most of the clays stays in the exfoliated or intercalated state. In the absence of intumescent, the cone calorimeter result shows that clay distance shrinks only 9.8 Å. Meanwhile, during the presence of intumescent agent, the cone calorimeter result shows 9.8 and 13.8 Å of clay distance. The morphological characterization was investigated by TEM analysis, and the result shows that intercalated and exploited clay was restacked while undergoing the cone calorimeter situation. The clay-organic intumescent hybrid system has a significant efficiency regarding the flammability properties of the EVA composite and reduction in the PHRR value. This phenomenon can be explained by the formation of a compact and aggregated dense clay–char layer as well as restacked clay during the combustion process.

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