

## Role of montmorillonite in flame retardancy of ethylene–vinyl acetate copolymer

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### Abstract

The effects of non-treated (MMT), organophilic (OMM), and olefin/silicone polymer intercalated (IMM) montmorillonites on the thermal stability of ethylene–vinyl acetate copolymer (EVA) and on the flammability of magnesium hydroxide filled EVA were studied. The influence of various treatments on the delamination of montmorillonites in EVA was detected by rheological measurements and by Raman microscopy. The latter was a unique method for rapid detection of the dispersion also in highly filled EVA. Enhancement of thermo-oxidative stability of EVA and flame-retarded EVA could be observed by thermal analysis in the presence of variously treated montmorillonites. The flame-retardant efficiency of magnesium hydroxide was improved by simultaneous application of MMT and IMM. The increased performance of magnesium hydroxide was explained by the rheological effect of the IMM, catalytic effect of MMT and chemical interactions of montmorillonites with the metal hydroxide.

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### 1. Introduction

Flame-retarded ethylene–vinyl acetate is a widely used material particularly in the cable industry. To achieve the required flame-retardant grade of low smoke and non-toxic character, metal hydroxides, mainly aluminium trihydroxide (ATH), are added in a high loading level. The basically excellent processing property of EVA, however, is degraded by the high amount of additive. One possible way to reduce the necessary amount of additive is to increase its flame-retardant effectiveness. Some earlier proposals are known for increasing the flame retardancy of metal hydroxides, such as adding Zn borate [1] or coating with Mo compound [2] or Zn hydroxy stannate [3] or boroxosiloxane [4]. Recently, considerable improvement in flame retardancy is expected from the combined addition of modified layered silicates and traditional flame retardants such as ammonium polyphosphate [5–7] or metal hydroxide [8,9]. The metal hydroxides during their flame-

retardant action evolve water vapour in an endothermic process. The vapour foams the melted polymer and, in the case of EVA matrix, disrupts the protective cross-linked layer formed from the unsaturated ethylene bonds of the deacetylated part of the matrix. An improved barrier layer was expected from the combined application of modified layered silicate and ATH. The synergetic effect of nanoparticles in the formation of barrier layer owing to the acceleration of the deacetylation, and to the migration of nanoparticles (forced by thermal degradation of their compatibilising agent) could be realized, but the destruction of the barrier layer of EVA by water could not be avoided [10]. It has also been established that total exfoliation is not essential in the improvement of the flammability and mechanical properties. It is in accordance with the observations of some other studies which used different surface treated synthetic and natural layered silicates [11,12].

In this work the effects of non-treated, organophilic, and olefin/silicone polymer intercalated montmorillonites on the thermal stability, flammability and mechanical properties of

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ethylene–vinyl acetate copolymer (EVA) and magnesium hydroxide filled EVA were investigated. The effects were explained based on the results of rheological, X-ray, Raman microscopic and thermo-analytical measurements.

## 2. Experimental

### 2.1. Materials

Non-modified Na-montmorillonite (MMT), Microtec (Eurotrade Ltd. Hungary); organophilic montmorillonite, Bentone SD-1 (OMM), a montmorillonite coated with long chain alkyl amine (Rheox. Inc.); polybutene/polysiloxane intercalated OMM (IMM), a laboratory product, prepared by solvent method; magnesium hydroxide ( $\text{Mg}(\text{OH})_2$ ) (Dead Sea Bromine Group); and ethylene–vinyl acetate copolymer (EVA), IBUCCELL K 100 with vinyl acetate content of 28% (H.B. Fuller) were investigated.

### 2.2. Preparation

The compounds were prepared in a Plasti Corder PL2000 type internal-mixer (Brabender) with rotor speed of 180 rpm at 180 °C in 10 min. Sheets ( $120 \times 120 \times 2$  mm) were obtained by compression moulding using Collin P 200 E type laboratory press at 180 °C and a pressure of 5 MPa. The composition of the prepared compounds is given in Table 1.

### 2.3. Characterization

Thermal decomposition of the compounds was analysed by thermogravimetric analysis (TGA) on a Setaram Labsys TG DTA/DSC instrument. Sample weight was about 15 mg, and the heating rate was 10 °C/min from 25 to 600 °C in air atmosphere.

The flammability was characterized by UL 94 test (ASTM 1356-90 and ANSI//ASTM D-635/77) and limiting oxygen index measurement (LOI, ASTM D 2863).

Tensile strength and elongation at break were measured by an Instron 1195 machine. The required test sample was of  $120 \times 10 \times 2$  mm size and the crosshead speed was 10 mm/min.

Table 1  
Composition of the prepared compounds

Components	Weight ratio
EVA	1
EVA and MMT	8:1
EVA and OMM	8:1
EVA and IMM	8:1
EVA, MMT and IMM	16:1:2
EVA and $\text{Mg}(\text{OH})_2$	1:1
EVA, $\text{Mg}(\text{OH})_2$ and MMT	8:8:1
EVA, $\text{Mg}(\text{OH})_2$ and OMM	8:8:1
EVA, $\text{Mg}(\text{OH})_2$ and IMM	8:8:1
EVA, $\text{Mg}(\text{OH})_2$ , MMT and IMM	16:16:1:2

Rheological data were collected by AR 2000 Thermal Scanning Rheometer (TA Instruments) in a parallel plate configuration. Samples of  $25 \times 25 \times 2$  mm size were positioned between the plates. The isothermal method was performed at 210 °C with torsion frequency from 1 to 600 rad/s at a starting gap of 1 mm. In the case of oscillation method the samples were heated from 130 to 550 °C with a heating rate of 15 °C/min at 8 Hz.

Raman imaging was performed by a LabRam type confocal Raman microscope (Jobin Yvon, France). The used magnification was 100 and the excitation source was frequency doubled Nd-YAG laser emitting at 532 nm.

X-ray diffraction analysis was carried out using a Philips diffractometer model PW 1050 with  $\text{CuK}_\alpha$  radiation.

## 3. Results and discussion

Two series of compounds were prepared. The first series contained only EVA and variously modified montmorillonites and served to demonstrating the effect of modification on the distribution of montmorillonite and on the mechanical properties of compound. The second series also contained  $\text{Mg}(\text{OH})_2$  and served to demonstrating the effect of modification on the flame retardancy, thermal behaviour and mechanical properties of compositions.

### 3.1. Dispersion and exfoliation

Organo-clay melt-blended in EVA containing 28% vinyl acetate comonomer exfoliate extensively, while in EVA containing low amount of vinyl acetate monomer only a moderate exfoliation and intercalation can be observed [13]. The dispersion degree of the clay mineral can be well demonstrated by the rheological behaviour. The high quality dispersion of nanocomposite, with exfoliated structure, shows intense viscosity change when the shear rate is changed, while a poorer dispersion gives rise to moderate change.

The rate of exfoliation of compounds containing only the variously modified montmorillonites was estimated by the measurement of the complex viscosity as a function of oscillation frequency [14]. The slope of curves, the so-called “shear thinning exponent” is able to show the extent of exfoliation of the montmorillonites. The higher the value of the exponent the higher the rate of exfoliation (Fig. 1).

The absolute values of the shear thinning exponents decrease in the following order: EVA–OMM  $\gg$  EVA–IMM > EVA–MMT–IMM  $\cong$  EVA–MMT = 0.84  $\gg$  0.56 > 0.46–0.45.

Based on these values the EVA containing OMM shows the highest exponent, consequently it must have the highest degree of exfoliation. This is in accordance with the optical appearance of the thin films of the compounds, as they showed a transparent, semi-opaque and dusty opaque transparency in the order of compounds mentioned above.

Direct information on the arrangement of montmorillonite particles is gained from the X-ray diffraction tests of the

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