

## **NONISOTHERMAL THERMOGRAVIMETRY OF POLYMERS**

### **IV. Polyethylene and ethylene-vinyl acetate copolymers highly loaded with $\text{Al}(\text{OH})_3$ and $\text{Mg}(\text{OH})_2$**

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#### **Abstract**

The decomposition of polyethylene and ethylene-vinyl acetate copolymers in composites with  $\text{Al}(\text{OH})_3$  and  $\text{Mg}(\text{OH})_2$  (60% by wt.) has been estimated from the aspect of the extent of synchronization of the two fundamental processes, the release of water and flammable volatiles from a polymer and the effect of this on the resulting polymer flammability. An attempt has been made to implement the peculiarities of decomposition observed for each system to the fire behaviour of these materials.

**Keywords:** copolymers, ethylene-vinyl acetate, flammability, LOI, polyethylene, TG

#### **Introduction**

Aluminium hydroxide and magnesium hydroxide have recently attracted appreciable attention because of their potential use in the fire retardance of thermoplastic and elastomer polymers [1, 2]. The study of decomposition of a polymer into volatile products in the presence of these additives, and vice versa, the decomposition of additives in the presence of a polymer, is of considerable interest, since it may clarify certain controversial ideas concerning interpretation of the effect of an inorganic matrix on polymer materials.

The present paper deals with the results of nonisothermal thermogravimetry for polyethylene (PE) and ethylene-vinyl acetate copolymers (EVA) loaded with 60% by wt. of  $\text{Al}(\text{OH})_3$  and  $\text{Mg}(\text{OH})_2$ .

A complete analysis of nonisothermal thermogravimetry curves obtained at different rates of sample heating in nitrogen and in air is put forward, and possible relations concerning the flammability of these samples, characterized by the limiting oxygen index (LOI), are discussed.

## Experimental

The PE used was very low-density polymer (melt index 0.9 g/10 min, density 0.9 g/cm<sup>3</sup>); the ethylene-vinyl acetate copolymer contained 50% of vinyl acetate groups (about 37.5% of acetic acid). The Mg(OH)<sub>2</sub> was the Kisuma 5A sample, and the Al(OH)<sub>3</sub> was an analytical grade powder.

Composites of Al(OH)<sub>3</sub> and Mg(OH)<sub>2</sub> were prepared on a calender. Samples were moulded at 130°C. Composites with EVA copolymer were mixed in a Plastograph Brabender, to which dicumyl peroxide was also added (1% by wt.) and samples were crosslinked by molding at 170°C for 12 minutes.

Decomposition of samples into volatiles was measured on a Derivatograph 1500 D (Hungary) with an adapter allowing work in different atmospheres. The initial sample mass was 50 mg, the rate of heating was from 2.5 to 10 deg·min<sup>-1</sup>, and experiments were carried out in nitrogen and air with a flow rate of 6 l/h.

Specific heats  $c_p$  of samples were measured on a Perkin-Elmer DSC 2 calorimeter in nitrogen atmosphere.

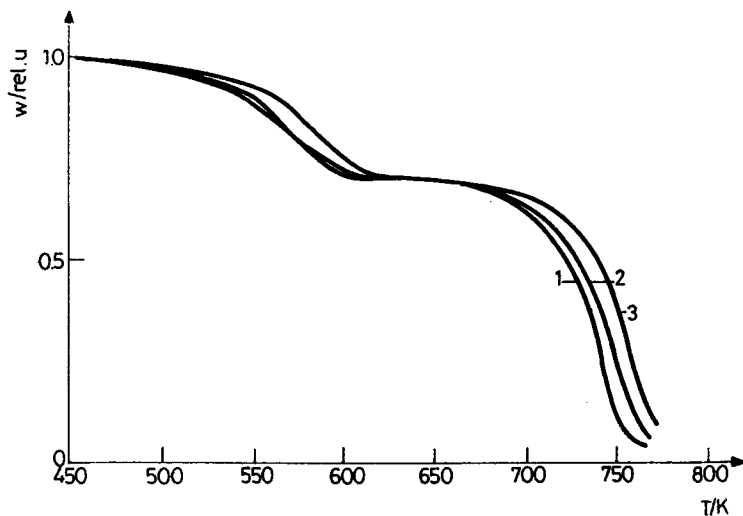
Nonisothermal TG curves were analyzed as being composed of one, two or three independent waves by a procedure described elsewhere [3] and parameters corresponding to each wave, such as apparent activation energy, preexponential factor and fraction, were evaluated. The apparent order with respect to each component was assumed to be 1.

## Results and discussion

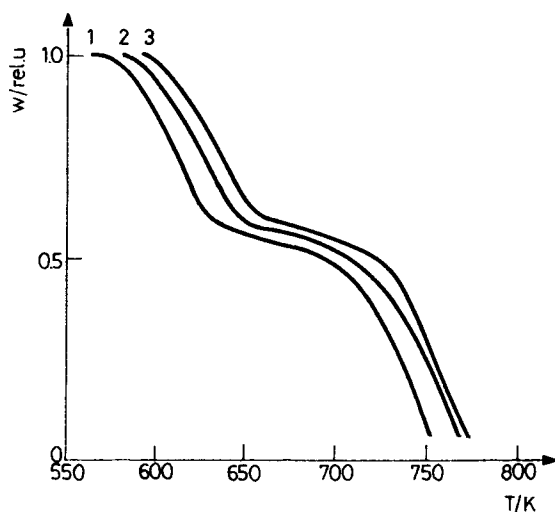
The representative pictures of decomposition into volatiles of the system consisting of 60% by wt. of Mg(OH)<sub>2</sub> and Al(OH)<sub>3</sub> and PE or EVA copolymer in nitrogen atmosphere are shown in Figs 1 and 2, respectively.

In the case of PE, the release of water from both Al(OH)<sub>3</sub> and Mg(OH)<sub>2</sub> precedes the formation of volatiles from the polymer, while acetic acid from the EVA copolymer induces the decomposition of Mg(OH)<sub>2</sub>. Most of the systems studied can be described by the superposition of two waves: the wave of water (or water with acetic acid) and that of products of polymer decomposition, Al(OH)<sub>3</sub> in the EVA copolymer behaves as being composed of three waves. Parameters obtained by analysis of nonisothermal TG records of the respective

systems (the apparent activation energy, the preexponential factor and the fraction  $\alpha$  of total volatiles corresponding to a respective wave) are listed in Tables 1–3. The theoretical amount of water in the volatiles is 34.2% for



**Fig. 1** Formation of volatiles from the system PE + Al(OH)<sub>3</sub> as measured by thermogravimetry in nitrogen atmosphere. Rate of heating 2.5 (1), 5 (2) and 10 (3) deg·min<sup>-1</sup>, initial weight of sample 50 mg



**Fig. 2** Formation of volatiles from the system EVA copolymer + Mg(OH)<sub>2</sub> as determined by thermogravimetry in nitrogen atmosphere. Rate of heating 2.5 (1), 5 (2) and 10 (3) deg·min<sup>-1</sup>, initial weight of sample 50 mg

PE + Al(OH)<sub>3</sub> (60% by wt.) and 32.1% for PE + Mg(OH)<sub>2</sub>. The value of  $\alpha_1$  (the fraction of volatiles corresponding to the first TG wave) for both systems, which lies between 27 and 33% by wt., indicates that in nitrogen atmosphere practically all the water escapes in a kinetically independent step.

As may be seen from the data in the Tables, the rate of heating does not have any particular effect on the values of the parameters obtained.

**Table 1** Parameters of decomposition of individual components of composites of PE and EVA copolymers with Al(OH)<sub>3</sub> and Mg(OH)<sub>2</sub> as found from nonisothermal thermogravimetry experiments

System		$\beta/$	$E_1/$	$E_2/$	$\ln(A_1/\beta)$	$\ln(A_2/\beta)$	$\alpha_1$	$\alpha_2$
		deg·min <sup>-1</sup>	kJ·mol <sup>-1</sup>					
Al(OH) <sub>3</sub>	N <sub>2</sub>	10	112	–	21.0	–	1.00	–
Mg(OH) <sub>2</sub>	N <sub>2</sub>	10	185	–	29.4	–	1.00	–
EVA	N <sub>2</sub>	10	167	264	29.0	39.9	0.32	0.68
EVA	air	10	151	117	25.9	14.4	0.34	0.66
PE	N <sub>2</sub>	10	195	–	27.2	–	1.00	–

Index 1 stands for the first wave, 2 for second wave of corresponding nonisothermal thermogravimetry record.

The apparent activation energy for the decomposition of Al(OH)<sub>3</sub> into water and Al<sub>2</sub>O<sub>3</sub> is about 80–100 kJ/mol, while that for Mg(OH)<sub>2</sub> is about 260 kJ/mol.

Either Al(OH)<sub>3</sub> or Al<sub>2</sub>O<sub>3</sub> reduces the apparent activation energy of decomposition of PE as compared with Mg(OH)<sub>2</sub> or MgO.

The fact that acetic acid formed in EVA copolymer decomposition induces the decomposition of Mg(OH)<sub>2</sub> may be documented by the value of  $\alpha_1$ . The experimental value of  $\alpha_1$  is 0.44, while the theoretical sum of the acetic acid and water fractions is 0.449. Problems of interpretation, however, may arise with the system of EVA copolymer with Al(OH)<sub>3</sub>. This behaves as if water were partly released independently and partly due to the effect of acetic acid on Al(OH)<sub>3</sub>, as a base. On extracting the respective waves from the experimental TG records and plotting them on a 100% scale each, we can see that the first wave with very low activation energy is spread over the whole temperature interval 450–800 K in which the decomposition of the system into volatiles was measured (Fig. 3). A very sharp release of some products, as depicted by the third wave, can hardly be understood as a process governed by chemical kinetic laws. It is interesting that oxygen from the air affects the first wave markedly (Fig. 3). This may lead to the assumption that extensive carbonization of

crosslinked EVA takes place due to  $\text{Al}_2\text{O}_3$ ; in air, this carbon residue is steadily oxidized within the  $\text{Al}_2\text{O}_3$  pores. In nitrogen atmosphere, the carbonized layer may keep some products of polymer decomposition encapsulated in the  $\text{Al}_2\text{O}_3$  mass. Thermomechanical destruction of the layer should result finally in an abrupt release of these products, which gives a very high apparent activation energy for this third wave.

It is worthwhile to discuss the relatively slight reduction in the apparent activation energy of  $\text{Al}(\text{OH})_3$  decomposition ( $\approx 80$  kJ/mol) when it is mixed with PE as compared with that for pure  $\text{Al}(\text{OH})_3$  (110 kJ/mol), while for  $\text{Mg}(\text{OH})_2$  the situation is the opposite (Tables 2 and 3). The apparent activation energies of PE decomposition in blends with  $\text{Al}(\text{OH})_3$  and  $\text{Mg}(\text{OH})_2$  are higher than that for the pure polymer, the latter case being much more pronounced. In terms of the interpretation proposed in papers [4, 5], this may be caused by a preferential termination of free radicals occurring on the inorganic surface via a first-order mechanism.

**Table 2** Parameters of individual waves of high temperature 'volatilization' of PE filled with  $\text{Al}(\text{OH})_3$  and  $\text{Mg}(\text{OH})_2$  (60% w.) as found from nonisothermal thermogravimetry experiments

System		$\beta/$ deg.min <sup>-1</sup>	$E_1/$ $E_2/$ kJ.mol <sup>-1</sup>		$\ln(A_1/\beta)$	$\ln(A_2/\beta)$	$\alpha_1$	$\alpha_2$
PE+Mg(OH) <sub>2</sub>	N <sub>2</sub>	2.5	224	281	37.9	43.5	0.32	0.68
		5.0	263	297	43.5	44.6	0.30	0.70
		10.0	260	278	42.6	41.1	0.27	0.73
PE+Al(OH) <sub>3</sub>	N <sub>2</sub>	2.5	79	229	13.0	34.3	0.32	0.68
		5.0	81	226	13.5	33.5	0.32	0.68
		10.0	79	244	12.6	35.9	0.33	0.67
PE+Mg(OH) <sub>2</sub>	air	2.5	219	370	36.0	58.5	0.48	0.52-
		5.0	211	356	34.0	54.7	0.46	0.54
		10.0	207	337	32.9	50.7	0.50	0.50
PE+Al(OH) <sub>3</sub>	air	5.0	64	165	9.0	22.9	0.44	0.56
		10.0	65	154	9.4	20.9	0.40	0.60

In air, the situation is different. The activation energy of  $\text{Al}(\text{OH})_3$  decomposition in the presence of PE is considerably lower than that for pure  $\text{Al}(\text{OH})_3$ ; that for  $\text{Mg}(\text{OH})_2$  and PE approaches the value for pure  $\text{Mg}(\text{OH})_2$ . The apparent

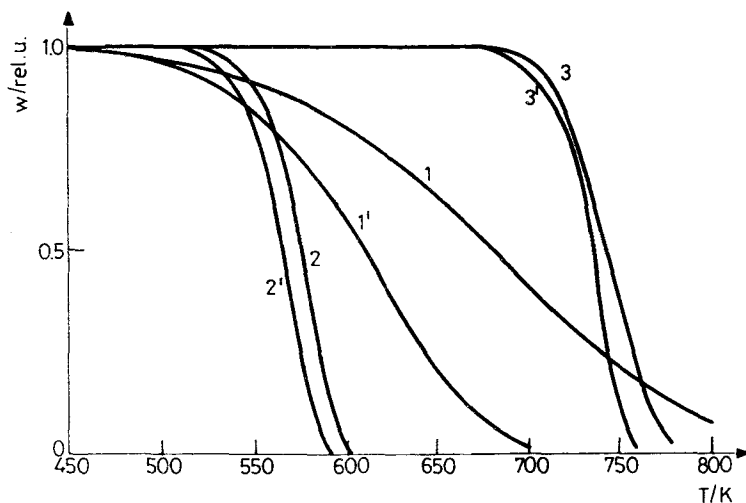
**Table 3** Parameters of individual waves of high temperature 'volatilization' of EVA copolymer filled with Al(OH)<sub>3</sub> and Mg(OH)<sub>2</sub> (60% w.) as found from nonisothermal thermogravimetry

System	$\beta$	$\text{deg}\cdot\text{min}^{-1}$			$\ln(A_1/\beta)$	$\ln(A_2/\beta)$	$\ln(A_3/\beta)$	$\alpha_1$	$\alpha_2$	$\alpha_3$	
		$E_1$	$E_2$	$E_3$							$\text{kJ}\cdot\text{mol}^{-1}$
EVA+Mg(OH) <sub>2</sub>	N <sub>2</sub>	2.5	188	255	—	33.9	33.8	—	0.44	0.55	—
		5.0	179	220	—	31.3	44.6	—	0.44	0.56	—
		10.0	188	244	—	32.7	35.9	—	0.43	0.57	—
EVA+Al(OH) <sub>3</sub>	N <sub>2</sub>	2.5	38	178	349	1.9	34.8	54.1	0.49	0.21	0.30
		5.0	35	160	344	1.5	30.6	52.7	0.41	0.20	0.39
		10.0	37	138	549	1.3	25.5	87.3	0.51	0.21	0.28
EVA+Mg(OH) <sub>2</sub>	air	5.0	175	196	—	24.5	41.6	—	0.54	0.44	—
		10.0	144	215	—	19.6	38.2	—	0.58	0.43	—
EVA+Al(OH) <sub>3</sub>	air	2.5	56	185	210	6.8	35.8	30.7	0.34	0.17	0.48
		5.0	48	185	273	4.9	35.7	40.9	0.44	0.16	0.41
		10.0	52	217	165	5.8	39.8	22.8	0.40	0.15	0.46

Index 1 stands for inorganic additive, 2 and 3 for polymer

activation energy of PE decomposition is reduced to about 150–160 kJ/mol for  $\text{Al}(\text{OH})_3$ , while that for  $\text{Mg}(\text{OH})_2$  reaches a relatively high value (around 350 kJ/mol).

In this latter case, the blanketing effect of water, the release of which coincides with the release of volatiles from the polymer, contributes to carbonization of the polymer, and the surface carbon layer formed can prevent free volatilization of the products of polymer decomposition until the layer is disrupted and the carbon residue is oxidized in a distinct exothermic process. The fraction of volatiles  $\alpha_1$ , which in nitrogen could be assigned to water only, is here larger by 16% wt. for PE +  $\text{Mg}(\text{OH})_2$  and by 10% for PE +  $\text{Al}(\text{OH})_3$ . The fact that in air a proportion of the flammable volatiles escapes together with water appears to be one of the reasons for the lowered flammability of thermoplastics heavily charged with  $\text{Mg}(\text{OH})_2$  and  $\text{Al}(\text{OH})_3$ .



**Fig. 3** Separation of individual waves for TG record of the system  $\text{Al}(\text{OH})_3$  + EVA copolymer in nitrogen (lines 1, 2 and 3) and in air (lines 1', 2' and 3'). All waves are related to 1. The rate of heating  $2.5 \text{ deg}\cdot\text{min}^{-1}$ , initial weight of sample 50 mg

The question remains as to which of these two inorganic additives is the better fire retardant in a particular polymer. Paper [6] gives the values of LOI 40 and 33 for EVA copolymers and  $\text{Al}(\text{OH})_3$  and  $\text{Mg}(\text{OH})_2$ , respectively. On the other hand, our results [7, 8] indicate that for PE and 60% by wt. of  $\text{Mg}(\text{OH})_2$  and  $\text{Al}(\text{OH})_3$ , both additives give about the same value of 29, while for the EVA copolymer  $\text{Mg}(\text{OH})_2$  appears to be considerably more efficient than  $\text{Al}(\text{OH})_3$  (LOI = 46 vs. 37). Keating and others [1, 2] report values of 31 for 60% of  $\text{Al}(\text{OH})_3$  and PE, and 37 for  $\text{Mg}(\text{OH})_2$  and PE. Regardless of some uncertainty

concerning the method of LOI determination for material with a large content of inorganic material, it seems that the resulting LOI values are determined primarily by the shape of the additive particles and also by their size. As reported by Hornsby [9], LOI for 60% by wt. of  $\text{Mg}(\text{OH})_2$  in PP composites varies in the interval 25–29%, depending on the regularity of the filler particles. Our experiments demonstrate that the larger fraction of flammable volatiles escaping together with water, as in the case of the  $\text{Mg}(\text{OH})_2$  + PE system in air, predetermines that  $\text{Mg}(\text{OH})_2$  is a better flame retardant for PE than  $\text{Al}(\text{OH})_3$ . This is also consistent with the longer times to ignition for samples containing  $\text{Mg}(\text{OH})_2$  than for those containing  $\text{Al}(\text{OH})_3$ . On the other hand, the apparent activation energy of decomposition of a polymer into volatiles, which determines the way in which flammable volatiles are supplied to the gaseous phase, can have an opposite effect. As found from a theoretical modelling of polymer ignition and burning [10], the higher values of polymer decomposition into flammable volatiles condition the lower values of LOI and vice versa; from this viewpoint, the use of  $\text{Al}(\text{OH})_3$  is more favourable.

From the temperature dependence of  $c_p$  for  $\text{Al}(\text{OH})_3$  and  $\text{Mg}(\text{OH})_2$  (Fig. 4), where  $c_p$  for  $\text{Mg}(\text{OH})_2$  is less than  $c_p$  for  $\text{Al}(\text{OH})_3$ , we may state that  $\text{Mg}(\text{OH})_2$  is a more efficient heat sink than  $\text{Al}(\text{OH})_3$ .

The evident effects of  $\text{Mg}(\text{OH})_2$  and  $\text{Al}(\text{OH})_3$  on smoke suppression in the burning of PE and PP, and also the distinct exothermic reaction occurring in the solid phase for the system PE and  $\text{Mg}(\text{OH})_2$  or  $\text{Al}(\text{OH})_3$  when exposed to tem-

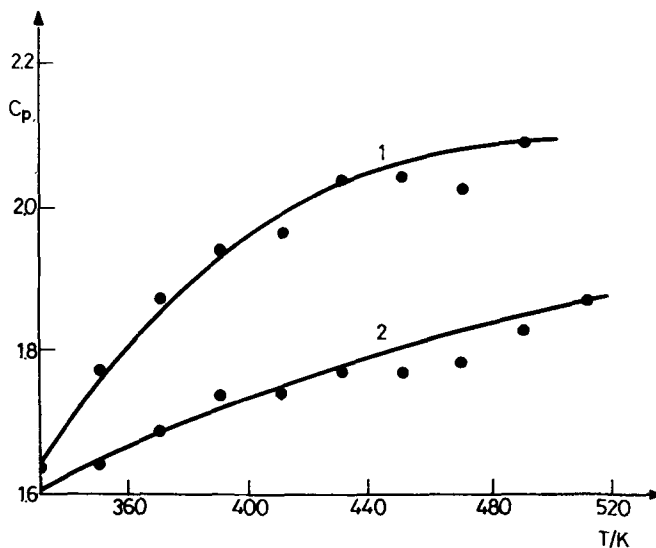
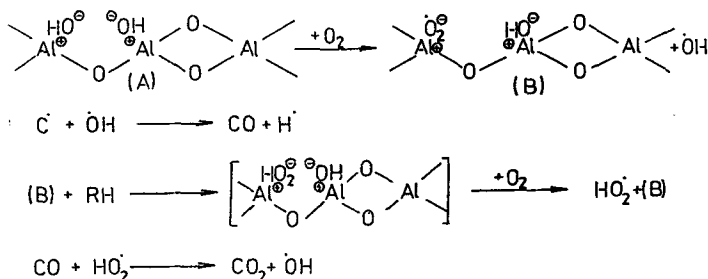


Fig. 4 Temperature dependence of  $c_p$  for  $\text{Al}(\text{OH})_3$  (1) and  $\text{Mg}(\text{OH})_2$  (2).  $c_p$  is in J/g.deg



peratures above 400°C and air, leads to the consideration of some catalytic effect of surface oxides on the oxidation of the carbonaceous residue. The fact that a few percent of water (from 3 to 5) remains in the oxide even after heating of the hydroxide above 500°C may justify the assumption that the catalytic effect of the oxides on the oxidation of polymer chars is due to residual hydroxy groups. The mechanism which we propose is based on a shuttle of electrons between hydroxy anion and air oxygen on the surface, with the sequence of reactions taking place as follows:



At a lower degree of polymer charring and a higher concentration of radicals  $R$ , these sites can play the role in radical termination changing the apparent order of termination of free radicals to lower values, which brings about an increased apparent activation energy of polymer decomposition. Comparison of the activation energies for decomposition of the individual components of the system into volatiles, as determined for a formal order of termination 1 (this paper) and those determined for an order 0.5 [7], confirms such an idea (Table 4). Reduction of the formal order of termination decreases the apparent activation energy of polymer decomposition significantly, while the activation energy for decomposition of the inorganic additive changes only slightly.

**Table 4** Comparison of activation energies for different formal orders of termination as found for some composite systems in air at the rate of heating 10 deg·min<sup>-1</sup>

System	Formal order of termination	$E_1/$	$E_2/$	Notice
		kJ·mol <sup>-1</sup>		
PE+Mg(OH) <sub>2</sub>	0.5	239	210	paper <sup>7</sup>
	1.0	207	337	this paper
PE+Al(OH) <sub>3</sub>	0.5	51	92	paper <sup>7</sup>
	1.0	65	154	this paper

Index 1 stands for inorganic additive, 2 stands for polymer

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**Zusammenfassung** — Die Zersetzung von Polyethylen- und Ethylvinylacetat-Kopolymeren in Gemischen mit  $\text{Al}(\text{OH})_3$  und  $\text{Mg}(\text{OH})_2$  (60 Gew.%) wurde unter dem Aspekt des Ausmaßes der Synchronisierung der zwei grundlegenden Prozesse beurteilt: der Freisetzung von Wasser und entzündlichen flüchtigen Substanzen aus dem Polymer und der dessen Effekt auf die Entzündlichkeit des resultierenden Polymers. Es wurde ein Versuch unternommen, die für jedes System beobachteten Besonderheiten der Zersetzung beim Feuerverhalten dieser Materialien anzuwenden.