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BRAZILIAN CLAYS AS SYNERGISTIC AGENTS IN AN ETHYLENIC POLYMER MATRIX CONTAINING AN INTUMESCENT FORMULATION

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The effect of two different Brazilian montmorillonitic clays in intumescent ammonium polyphosphate and pentaerythritol formulations was evaluated. Ethylene and butyl acrylate copolymer was used as polymeric matrix. The clays were added both to the pure polymer and to the polymer containing intumescent mixture. The influence of these mineral fillers on flame retardancy was investigated by thermogravimeric analysis (TG). The results show that these inorganic additives have a synergist effect in the polymeric composite containing the intumescent formulation.

Keywords: *flame retardancy, intumescent formulations, TG*

Introduction

A constant demand for flame retarding systems in the polymer industry that they should be environmentally more friendly than the widely used organohalogenated compounds. The development of intumescent formulations is amongst the various alternatives studied. The flame retarding mechanism of intumescent formulations is based on the formation of a tumid carbonaceous surface layer with cellular structure called to ‘char’. This structure protects the underlying polymer from flame incidence, lowers the heat transfer coefficient between the flame and the polymeric material, limits oxygen diffusion to the polymer and reduces the mass transfer of the pyrolysis products that fuel the flame. An intumescent formulation generally contains three active components [1]: a) an acid source, such as ammonium polyphosphate (APP) that generates a mineral acid with temperature increase; b) a carbonific agent, usually polyhydroxylated organic compounds, like pentaerythritol (PER), which will react with the acid formed by the acid source to generate the char; c) a blowing agent which releases non-flammable gaseous compounds that are responsible for the swelling of the carbonaceous layer. APP can function as both the acid source and the blowing agent, since it releases ammonia around 150°C. Bourbigot *et al*. [2–5] developed intumescent systems using zeolites and clays as synergistic agents, and have achieved some very promising results. In this study, two Brazilian montmorillonitic clays, here forth denominated clays M and V were evaluated as possible synergistic agents in APP/PER intumescent formulations. Thermogravimetric analysis (TG) was used to assess the flame retardancy potential of the produced systems. This technique has been adequately used to study the fire resistance of various matrices and flame retardants [6, 7] including flame retardants based on phosphorus compounds [8].

Experimental

The used polymer matrix consisted of an ethylene and butyl acrylate copolymer containing 30 mass% of butyl acrylate (EBA30), supplied by Elf-Atochem. The intumescent additives used were APP supplied by Clariant under the trade name Exolit AP 422, and PER, from Sigma Aldrich. The APP:PER ratio was kept constant at 3 where, according to the literature, maximum fire retarding properties are observed for ethylenic materials [2].

The clays were submitted to mechanical sifting, and the fractions that passed through the 212 μm standard sieve were collected for processing. The clays were added to the polymer in order to account for 3 mass% of the total mixture. The chemical and mineralogical compositions of the two clays are given in Table 1.

The polymer and the additives were mixed in a Haake Rheocord 9000 equipped with a 69 cm^3 rheomix chamber and Roller Blades rotors at 160°C with 50 rpm for 15 min. The mixture was then pressed in a Carver press applying a 20000 lbf load on a 10×10 cm area to obtain sheets with 3 mm thick.

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Table 1 Chemical and mineralogical compositions of the clays studied

Composition	Clay M/mass%	Clay V/mass%
Chemical[a]		
SiO_2	63.8	54.6
Al_2O_3	27.3	32.2
Fe_2O_3	5.9	5.8
K_2O	0.5	4.6
CaO	1.1	1.7
TiO_2	0.9	0.7
Mineralogical[b]		
Clay minerals and mica	45	65
Quartz	35	30
Plagioclase feldspar	5	–
Apatite	10	–
K-feldspar	5	5

[a]Determined by X-ray fluorescence; [b]determined by X-ray diffraction

The samples thus obtained were pulverized in cryogenic mill and submitted to TG measurements. The analyses were performed using a PerkinElmer Analysis System Series 7, where 10 mg of the samples were placed to a platinum microbalance pan and heated at 10°C min^{-1} heating rate under a synthetic air flow of 20 cm^3 min^{-1}. The temperature shifts and the residual mass after 850°C were regarded as an indication of the relative thermal stability.

The TG curves obtained for the pure components and/or for certain additive mixtures were used to calculate theoretical thermal degradation curves for a given sample. This method has been previously documented as a useful tool in characterizing synergistic effects between additives [2, 4, 9]. Deviations from the theoretical curves were regarded as indication of synergistic effects amongst the additives and between the additives and the polymeric matrix. The theoretical mass loss curves [$M_{th}(T)$] were calculated according to Eq. (2) shown in Table 2, where $M(T)$ are the experimental curves obtained for the subscript component(s).

Results and discussion

The difference in thermal behavior brought about by clay addition to the polymer is shown in Fig. 1. When mass loss reaches 70%, the obtained curves reveal a 70°C shift to higher degradation temperatures in the clay containing systems, when compared to the pure polymer. However, no significant difference in degradation profile is observed among the polymer–clay samples.

By adding the intumescent APP/PER mixture to the polymer, the degradation temperature is shifted to significantly higher values, as could be expected (Fig. 2). Clay addition to the polymer containing APP/PER formulation did not reveal temperature changes in mass loss associated phenomena. However, the amount of high temperature residue greatly increases by adding clay to the intumescent polymer mixture. The obtained amount of residue was greater than it would be expected considering the content of the inorganic material processed. Table 3 shows that the clays were able to increase the amount of stable residue at 850°C by 3-fold, relative to their original content. Although the ratio between the obtained residue ($W_{residue}$) and the clay content (W_{clay}) are very similar for the two clays used, there seems to be a tendency towards higher ratios for systems containing clay M.

Estevão *et al.* [10] verified that silica-aluminates are more efficient flame retardancy enhancers than either silica or alumina alone. Silica-aluminates seem to change the degradation pathway of APP/PER intumescent formulations, possibly leading to a glassy phosphate network. This glassy phosphate network modified by the presence of silicon and aluminum may also act as an additional insulating layer. Thus, it is expected that the amount of aluminum and silicon oxides can influence the extent of the synergistic effect in an intumescent system. This was indeed observed. Clay M has a higher SiO_2 and Al_2O_3 content (91.1%) than clay V (86.8%). This confirms that the SiO_2 and Al_2O_3 content play a major role in the extent of the synergistic effect amongst the various additives.

Many authors have sought a better understanding of the synergistic effect observed between various types of ammonium phosphates and hydroxylated compounds [11–15]. However, regardless the different reaction schemes proposed, it is widely believed that the intumescent process involves the formation of phosphate esters and the release of water and ammonia molecules. Camino *et al.* [12] and Marosi end Ravadits [13] have thoroughly investigated the classical APP/PER system. The first step seems to involve the phosphorylation of PER without the elimination of any

Table 2 Equations used to calculate the theoretical TG curves

Studied effect	Equations
Synergy between APP and PER	$M_{th}(T)=0.75M_{APP}(T)+0.25M_{PER}(T)$ (1)
Synergy between the clay and the APP/PER intumescent formulation	$M_{th}(T)=0.91M_{APP/PER}(T)+0.09M_{clay}(T)$ (2)
Synergy between the clay and the polymer	$M_{th}(T)=0.97M_{poly}(T)+0.03M_{clay}(T)$ (3)
Synergy between the clay and the intumescent polymer mixture	$M_{th}(T)=0.67M_{poly}(T)+0.30M_{APP/PER}(T)+0.03M_{clay}(T)$ (4)

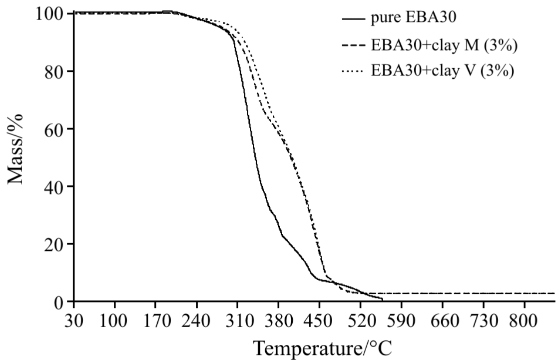

Fig. 1 Experimental TG curves of the pure polymer and of polymeric formulations with mineral fillers

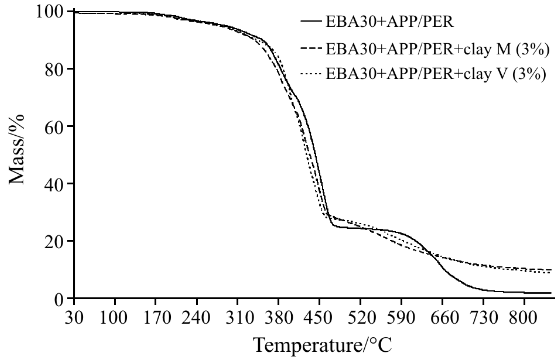

Fig. 2 Experimental TG curves of the intumescent polymeric formulations with and without clay addition

gaseous products, followed by the formation of cyclic phosphate ester structures with the elimination of ammonia and water. Intumescence takes place at temperatures around 350°C when P–O–C bonds undergo thermal scission with the formation of a voluminous char impregnated by polyphosphoric acids. Bourbigot [5], while studying APP/PER in ethylenic copolymeric matrices proposed that the polyphosphoric acid generated by ammonia release can react both with the PER and with the hydroxyls generated from the breakdown of the polymer chains in the matrix.

Despite all discussion on the mechanism of the intumescent process involving APP and PER, the synergistic effect between these additives is undeniable. This is clearly shown in Fig. 3 where the theoretical curve was obtained using Eq. (1), Table 2. The theoretical curve calculated by the linear combination of the experimental curves for individual additives represents the degradation of the mixture when no interaction between the additives occurs. Comparing the theoretical APP/PER curve with the experimental curve it can be observed that the latter has been shifted to higher temperatures reflecting the well known synergistic effect between the additives. It is then clear that comparing experimental and theoretical curves can adequately detect synergy amongst the components in an intumescent formulation.

Table 3 Ratio between the amount of high temperature residue at 850°C and mineral filler concentration determined by TG (The analyses were carried out in triplicates)

Mixture	$W_{\text{residue}}/W_{\text{clay}}$
EBA30+APP/PER+clay M 3%	3.12±0.19
EBA30+APP/PER+clay V 3%	2.85±0.27

Following the same procedure of comparing experimental and theoretical curves, several synergistic effects can be detected in the studied systems. Figures 4 and 5 reveal that the montmorillonitic clays also show considerable synergy with APP/PER.

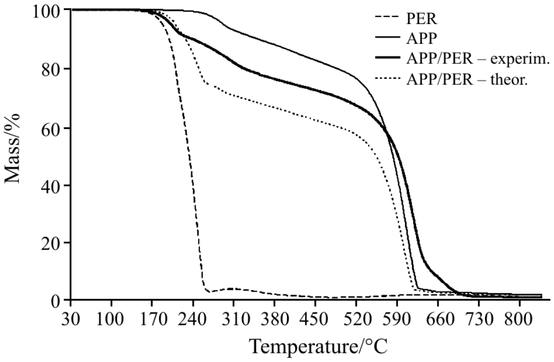

Fig. 3 Experimental and theoretical TG curves of intumescent additives. Theoretical curve obtained from Eq. (1), Table 2

The next logical step would then be to determine if the montmorillonitic clay shows synergy with the EBA matrix and, as Fig. 6 shows for clay M, this is clearly the case. Similar profiles were also obtained for clay V. Hence, the clays studied show synergistic effect, regarding the thermal resistance of the materials with both the polymer matrix and the classical intumescent additives (APP/PER). The combined flame retardancy enhancing effect obtained from adding clay M to the complete polymeric intumescent formulation is shown in Fig. 7. The results show a pro-

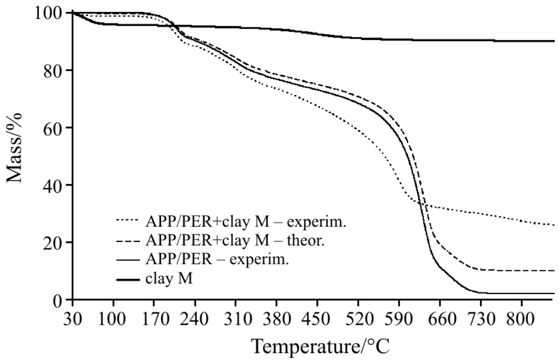

Fig. 4 Experimental and theoretical TG curves of APP/PER mixture with clay M. Theoretical curve obtained from Eq. (2), Table 2

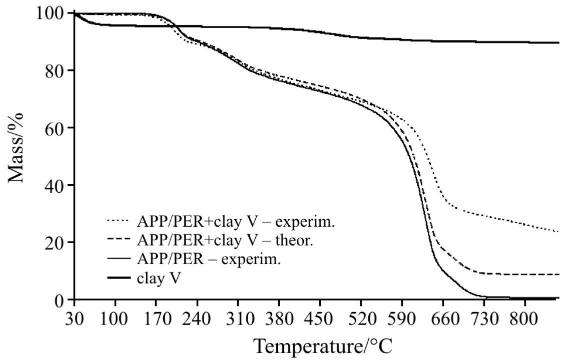

Fig. 5 Experimental and theoretical TG curves of APP/PER mixture with clay V. Theoretical curve obtained from Eq. (2), Table 2

nounced synergistic effect resulting in a shift to higher degradation temperatures and in an increase in high temperature residue in the experimental curves when compared to the theoretical ones. Once again, clay V revealed the same behavior as clay M.

While the mechanism for enhanced fire retardancy performance by clay addition is still not clear, a preliminary proposal, based on studies reported in the literature, could be that the clay platelets produce a multi-layered carbonaceous alumino silicate structure that acts as a barrier to heat and mass transfer [16]. The presence of iron in the clays may also contribute towards the additional stability of the mixtures, since it can lead to radical trapping, hence slowing down the exothermic chain reactions involved in the burning process [17].

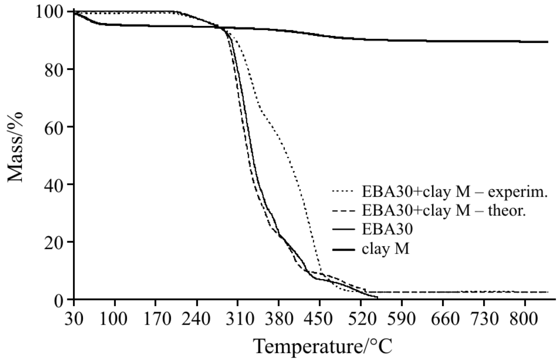

Fig. 6 Experimental and theoretical TG curves of EBA30 and clay M formulations. Theoretical curve obtained from Eq. (3), Table 2

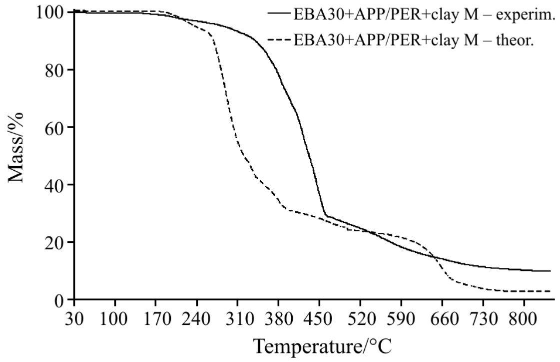

Fig. 7 Experimental and theoretical TG curves of the intumescent formulations with clay M. Theoretical curve obtained from Eq. (4), Table 2

Conclusions

Two Brazilian montmorillonitic clays with different chemical compositions were incorporated into APP and PER intumescent systems in an ethylene–butyl acrylate copolymer as matrix. The thermal stability of the clay-containing intumescent mixtures seems to depend on the silica-aluminate content. By using inorganic fillers with greater aluminum and silicon oxide content the produced materials exhibited a greater amount of high temperature residue. Synergistic effects were observed between the clays and the polymer matrix, the clays and the intumescent formulation, and in the complete flame retarding polymer formulation. Hence, the clays studied are liable to enhance the fire retardancy properties of intumescent APP/PER formulations and increase the thermal resistance of pure polymers.

References

1 M. Elomaa, L. Sarvaranta, E. Mokkola, R. Kallonen, A. Zitting, C. A. P. Zevenhoven and M. Hupa, Crit. Rev. Biochem. Mol. Biol., 27 (1997) 137.
2 S. Boubigot, M. Le Bras, P. Breant, J. M. Tremillon and R. Delobel, Fire Mater., 20 (1996) 145.
3 S. Boubigot and M. Le Bras, Fire Retardancy of Polymers: The use of intumescence. M. Le Bras, G. Camino, S. Bourbigot and R. Delobel, Eds, The Royal Society of Chemistry, Cambridge 1998, p. 222.
4 S. Bourbigot, M. Le Bras, R. Delobel, P. Bréant and J. M. Tremillon, Polym. Degrad. Stab., 54 (1996) 275.
5 S. Bourbigot, Les Zeolithes, Nouveaux Agents de Synergie dans les Systèmes Intumescents: Comprehension des Mécanismes de Protection du Polyethylene et de ses Copolymères, Ph.D. Thesis, University of Lille, 1993.
6 H. Polli, L. A. M. Pontes, M. J. B. Souza, V. J. Fernandes Jr. and A. S. Araújo, J. Therm. Anal. Cal., 86 (2006) 469.
7 V. M. Fonseca, V. J. Fernandes Jr., A. S. Araújo, L. H. Carvalho and A. G. Souza, J. Therm. Anal. Cal., 79 (2005) 429.
8 B. A. Howell and J. Uzibor, J. Therm. Anal. Cal., 85 (2006) 45.
9 M. Bugajny, S. Bourbigot, M. Le Bras and R. Delobel, Polym. Int., 48 (1999) 264.
10 L. R. M. Estevão, M. Le Bras, R. Delobel and R. S. V. Nascimento, Polym. Degrad. Stab., 88 (2005) 444.

11 G. Camino and L. Costa, Polym. Degrad. Stab., 20 (1988) 271.

12 G. Camino, L. Costa and G. Martinasso, Polym. Degrad. Stab., 23 (1989) 359.

13 G. Marosi, I. Ravadits, G. Bertalan, P. Anna and M. A. Maatoug, Fire Retardancy of Polymers: The Use of Intumescence, M. Le Bras, G. Camino, S. Bourbigot and R. Delobel, Eds, The Royal Society of Chemistry, England 1998, p. 325.

14 K. Kishore and K. Mohandas, Combust. Flame, 43 (1981) 145.

15 S. Duquesne, Etude des Procédés d'Ignifugation de Substrats Polymères par Revêtements Intumescents, Ph.D. Thesis, University of Lille, 2001.

16 J. W. Gilman, C. L. Jackson, A. B. Morgan, R. Harris Jr., E. Manias, E. P. Giannelis, M. Wuthenowet, D. Hilton and S. H. Phillips, Chem. Mater., 12 (2000) 1866.

17 J. Zhu, F. M. Uhl, A. B. Morgan and C. A. Wilkie, Chem. Mater., 13 (2001) 4649.

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