Metallic Oxides as Fire Retardants and Smoke Suppressants in Flexible Poly(Vinyl Chloride)

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ABSTRACT: Combustion and smoke emission properties of PVC compounds, modified with copper (II), molybdenum, and zinc oxides, were studied using cone calorimeter, limiting oxygen index (LOI) and thermogravimetry coupled with mass spectrometry (TG/MS). Results showed that the metal oxides have a very significant effect on the combustion and smoke suppression properties of the PVC compounds. The results also confirmed the anticipation mechanisms of the dehydrochlorination reactions, reductive coupling, and elimination of benzene resulting from the presence of copper (II), molybdenum, and zinc, indicated by the increasing content of postcombustion char residue and the significant reduction in benzene production, indicated by the MS measurements performed. The results also provide indications that the combination of the copper (II) and molybdenum oxides is the one with the best balance of combustion properties, as it reduced the heat released and promoted the suppression of smoke more efficiently. The formulations containing ZnO, because of their strong Lewis acid character, indicated a less pronounced reduction of smoke released during the combustion process, when compared with copper (II) and molybdenum oxides. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 118: 2613–2623, 2010

Key words: poly(vinyl chloride); flame retardance; composites

INTRODUCTION

Since its discovery, humans are exposed to risks that fire provides to its users,[1] one of the main attacks against the integrity of the human race. With the accelerated development of mankind in the 20th Century, the domiciles are more equipped, with a large number of combustible materials in them, such as furniture, carpets, coverings, and the most diverse electronic devices. In the same way, industry and commerce have larger number of goods produced and stored at the same site, many times surrounded by greater concentration of people in increasingly more vertical cities. In addition, new technologies are made available daily in the market, with new fire risk potential or new materials about which we do not have full knowledge.

To minimize the risks of the fire, the development of new materials resistant to combustion can be an important alternative to protect against human life loss and civil construction like hospitals, industries, houses, schools, libraries, shopping centers, and others.[2] When a sufficient amount of heat is supplied to any organic polymer, it decomposes thermally and leads to death by asphyxia.[3,4] In reality, the risk of life of a specific material, or component, under fire is a result of the combination of both flammability and the toxicity of gases released during its combustion,[5] and the rate at which these toxic gases are released.[6] Other risks inherent to a fire situation are the convective and radiant heat and the low-concentration of oxygen in the atmosphere, causing a narcotic effect by the combination of a high-concentration of carbon monoxide with a low-concentration of oxygen. These are the most important incapacitating factors for those trying to escape a place on fire.[7]

The presence of chlorine in PVC's chemical structure provides the benefits of low-flammability in products made with this polymer, but it also promotes a particular combustion mechanism that ends up generating a great amount of dense and dark smoke. This smoke is another important incapacitating factor when analyzing a specific fire condition[4]; therefore, controlling smoke emitted by PVC compounds is very important, and it is only achieved by adding smoke suppressing agents. Several smoke suppressing agents, including zinc, boron, tin, iron, and molybdenum compounds are commercially available.[8]

Electric cables always present a risk in fire situations because they often run through ducts that

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frequently cross through different compartments of a building and are installed in remote sites, hindering the access of people.[9] For this reason, improved performance of those materials used as insulation in electric wires and cables is important for the safety of the building and the people who work or live in it.

Smoke suppressors in PVC, based on molybdenum and copper, were previously studied by Starnes Jr. and coworkers,[10–15] Kroenke and Lattimer,[16–20] and Li and Wang.[21–26] In a previous work,[27] the authors presented the combustion and degradation properties of PVC/metallic oxides/O-MMT nanocomposites, and concluded that the effects of a ternary mixture of CuO/MoO$_3$/ZnO is significantly more efficient in the reduction of heat release and smoke suppression of a flexible PVC compound. Morley[8] also reports the commercial use of molybdenum and zinc compounds as smoke suppressors in PVC formulations, normally supported in inert fillers like calcium carbonate or talc. However, the study of the ternary interactions between copper, molybdenum, and zinc oxides as potential flame retardants and smoke suppressants in PVC formulations are not known in the academic community. The objective of this research is the study of these interactions between copper, molybdenum, and zinc oxides, on the dehydrochlorination process, combustibility, and smoke emission properties of flexible PVC compounds.

EXPERIMENTAL

Materials

The formulation of the PVC compound, taken as a reference and summarized in Table I, was based in common practices used in PVC cable transformers in Brazil. PVC resin with a K value of 65 ± 1 (Norvic SP 1000, Braskem S/A, Camaçari, Brazil) was used as the polymer matrix. The other components of the basic formulation are detailed in Table I and have been acquired from commercial sources. Table II shows complete details of the formulations assessed in this study, based on a simplex-centroid design of experiment (DOE).[28] Metallic oxides were supplied from commercial sources, and particle size was evaluated in a Mastersizer S-MAM 5005 analyzer (Malvern Instruments, Malvern, UK). Volumetric mean particle sizes were (4.83 ± 0.03) μm, (1.36 ± 0.02) μm, and (2.77 ± 0.16) μm for CuO, MoO$_3$, and ZnO, respectively. The metallic oxides were incorporated into the PVC formulation in a total amount of 5 wt %. In this specific DOE, the mathematical modeling allows the evaluation of the effects of the isolated substances and their binary and ternary interactions, following the model presented on eq. (1):

TABLE I
PVC Compound Formulation Used in this Study

Component	Amount (phr)
Norvic SP 1000 (PVC resin K 65)	100
Naftomix XC-1202 (Ca/Zn thermal stabilizer)	3.5
DIDP	45
Drapex 6.8 (ESO)	5
Barralev C (precipitated calcium carbonate)	40
Stearic acid	0.2

$$y = \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 + \beta_{12} x_1 x_2 + \beta_{13} x_1 x_3 + \beta_{23} x_2 x_3 + \beta_{123} x_1 x_2 x_3$$

(1)

Where y is the property to be modeled, β_1, β_2, and β_3 are first-order coefficients, respectively, of factors x_1, x_2 and x_3, β_{12}, β_{13} and β_{23} are coefficients for the binary interaction between factors x_1, x_2 and x_3, and β_{123} is the coefficient for the ternary interaction among factors x_1, x_2 and x_3.

Composition preparation

All formulations were homogenized through a Mecanoplast (Rio Claro, Brazil) ML-9 intensive mixer. Initially, the resin, the thermal stabilizer, the calcium carbonate, the stearic acid and, where applicable, the different metallic oxides were added to the mixer, at room temperature, and after being submitted to shear up to 80°C, the plasticizers DIDP and ESO were incorporated. The final composition was discharged at 110°C, following by cooling at 35 – 40°C to avoid the formation of agglomerates.

The formulations were then processed in a Miotto (São Bernardo do Campo, Brazil) LM 03/30 single screw extruder (30 mm, L/D 25), through the temperature profile of 140–145–150°C and 80 rpm. Test specimens were obtained from the pellets in a Mecanoplast laboratory two roll mill. The temperature, the processing time, and the rotation to prepare 3 mm-thick plates, from which the test specimens were taken, were 160°C, 3 min, and 20 rpm, respectively. The materials pressing was performed in a stainless steel Luxor (São Paulo, Brazil) press, at 175°C.

Combustion properties

The risk that a given material offers, when considering fire, depends on the combination of different factors, such as[3]: ignitability, ease of extinction, flame propagation, heat release, smoke obscuration, and toxicity of the smoke released.

TABLE II
Complete Description of the PVC Formulations Evaluated in this Study

Identification	PVC base compound (wt %)	CuO (wt %)	MoO$_3$ (wt %)	ZnO (wt %)
PVC	100	0	0	0
PVC-Cu	95	5	0	0
PVC-Mo	95	0	5	0
PVC-Zn	95	0	0	5
PVC-Cu-Mo	95	2.5	2.5	0
PVC-Cu-Zn	95	2.5	0	2.5
PVC-Mo-Zn	95	0	2.5	2.5
PVC-Cu-Mo-Zn	95	1.67	1.67	1.67

Combustion and smoke release properties of the compounds were assessed using different and complementary techniques. It is accepted as a current opinion[1,3,21–26,29–34] that the cone calorimeter technique is one of the most complete methodologies normally available to assess combustion and smoke release properties in a representative manner in a single, quick, and relatively simple test. Cone calorimeter measurements were made using a Stanton Redcroft – Fire Testing Technology (East Grinstead, UK) equipment according to the procedures described in ISO 5660-1, in specimens measuring 100 mm $\times$ 100 mm $\times$ 3 mm, in duplicate for each formulation, under an incident heat flux of 50 kW m^{-2} and a duct flow rate equal to 24 L s^{-1}. The specimens were protected by aluminum foil and propped on a ceramic support so that only the upper face was exposed to the radiant heat flux and subjected to 20°C and 30% relative humidity before testing.

The ease of extinction of the compounds was assessed through the Limiting Oxygen Index (LOI) test, according to ASTM D 2863-06a, using a fire testing technology equipment, in three specimens for each formulation. The tests were conducted at a temperature of (23 $\pm$ 2)°C and (50 $\pm$ 5)% relative humidity.

Electrical properties

The volumetric electrical resistivity of the samples was evaluated in an Agilent (Santa Clara, CA) 4339B high-resistance meter, equipped with a 16008 B resistivity cell, according to ASTM D257-07. Three test specimens of each formulation were evaluated, at (23 $\pm$ 2)°C, after conditioning for 40 h in distilled water.

Dynamic thermal stability

The dynamic thermal stability (under shear) of the compounds was evaluated in a torque rheometer from Thermo Haake (Karlsruhe, Germany) Polylab System, model Rheocord 300p, equipped with a Rheomix 610P mixer and roller rotors, and Polyview

2.1.1 software. The tests were carried out according to ASTM D2538-02, at 200°C, 90 rpm, and 62 g, in duplicate.

Thermogravimetry coupled to mass spectroscopy (TG/MS)

One of the objectives of this study was to assess the effects of metallic oxides on the dehydrochlorination and smoke release behavior of PVC nanocomposites, correlating chemical species released during the pyrolysis process and the effects observed in the cone calorimeter test. The different formulations were assessed as to stability to heat using a STA 409 thermobalance coupled to a QMS 403 mass spectrometer, both from Netzsch analyzing and testing (Selb, Germany), using alumina crucibles in a synthetic air atmosphere with a gas flow of 50 mL min^{-1}. Scans were conducted between room temperature and 1000°C, at a heating rate of 20°C min^{-1}. Samples for TG/MS were taken from the processed specimens.

Scanning electronic microscopy (SEM)

SEM observations were made using Philips XL 30 equipment (FEI Company, Hillsboro, OR), operated at 20 kV, equipped with an Edax energy dispersive X-ray spectroscope (EDS), model New XL 30. Analyzed samples were obtained from the compounds pyrolysis in a CEM (Matthews, NC) Phoenix Airwave microwave muffle furnace, at 600°C for 1 h. The ashes resulting from this process were covered with a thin carbon film using a Bal-Tec (Leica Microsystems, Wetzlar, Germany) SCD 005 sputter, operated at 60 mA and 10^{-1} mbar for 100 s, to allow the analysis of molybdenum through the EDS.

Statistical analysis

Statistical analyses were performed via Microsoft Excel. More sophisticate analyses, such as the evaluation of the effects of the different metallic oxides, were carried out with Minitab 15 (Minitab, Inc., State College, PA), as the formulations evaluated

TABLE III
Cone Calorimeter (50 Kw m⁻²) and LOI Results for PVC/Metallic Oxides Compounds

Formulation	PHRR (kW m^{-2})	MHRR (kW m^{-2})	THR (MJ m^{-2})	MEHC (MJ kg^{-1})	ASMLR (g s^{-1} m^{-2})	TSP (m^2 kg^{-1})	MCO (kg kg^{-1})	CR (%)	NCR (%)	LOI (%)
PVC	285 ± 11	130 ± 5	66.1 ± 0.1	18.5 ± 0.1	11.8 ± 2.3	736 ± 21	0.054 ± 0.004	26.0 ± 0.1	26.0 ± 0.1	23.0
PVC-Cu	192 ± 6	97 ± 2	51.1 ± 0.4	15.1 ± 0.0	10.3 ± 0.6	379 ± 21	0.074 ± 0.003	36.1 ± 0.1	34.3 ± 0.1	24.4
PVC-Mo	208 ± 5	100 ± 7	46.4 ± 2.1	15.6 ± 0.8	10.5 ± 0.3	392 ± 3	0.052 ± 0.004	35.6 ± 0.3	33.8 ± 0.2	26.6
PVC-Zn	273 ±3	105 ± 9	48.2 ± 3.9	13.9 ± 0.4	12.9 ± 0.4	517 ± 1	0.066 ± 0.003	33.5 ± 1.1	31.8 ± 1.0	24.7
PVC-Cu-Mo	188 ± 1	99 ± 10	44.8 ± 2.0	15.1 ± 0.6	10.8 ± 0.2	365 ± 2	0.065 ± 0.002	36.9 ± 0.9	35.0 ± 0.9	26.4
PVC-Cu-Zn	240 ± 11	131 ± 3	69.9 ± 19.3	20.6 ± 4.9	11.6 ± 1.8	437 ± 2	0.064 ± 0.002	34.5 ± 2.2	32.8 ± 2.1	24.3
PVC-Mo-Zn	199 ± 5	109 ± 2	48.8 ± 1.9	15.9 ± 0.6	11.3 ± 0.2	492 ± 11	0.056 ± 0.002	34.9 ± 0.8	33.2 ± 0.8	24.5
PVC-Cu-Mo-Zn	191 ± 15	100 ± 3	44.6 ± 1.6	14.1 ± 0.1	12.0 ± 0.8	387 ± 13	0.060 ± 0.000	37.3 ± 0.5	35.4 ± 0.5	26.4
Regression analysis (Minitab® 15)										
Model (*p*-value)	0.000	0.001	0.024	0.022	0.026	0.000	0.000	0.015	0.013	-
Linear (*p*-value)	0.000	0.236	0.702	0.472	0.005	0.000	0.000	0.025	0.024	-
Binary (*p*-value)	0.000	0.001	0.017	0.008	0.698	0.001	0.012	0.415	0.387	-
Ternary (*p*-value)	0.039	0.003	0.047	0.017	0.196	0.000	0.781	0.043	0.037	-
Model R^2 (adjusted)	0.9665	0.8655	0.6604	0.6694	0.6496	0.9835	0.9336	0.7064	0.7165	-

Cone calorimeter parameters: PHRR - Peak Heat Release Rate; MHRR - Mean Heat Release Rate; THR - Total Heat Released; MEHC - Mean Effective Heat of Combustion; ASMLR - Average Specific Mass Loss Rate; TSP - Total Smoke Production; MCO - Mean CO; CR - Char Residue; NCR - Normalized Char Residue. For a detailed description of these parameters please see reference.[21]

correspond to a simplex-centroid mixture design of experiment.

RESULTS AND DISCUSSION

Combustion properties

Table III shows a summary of the main measurement results taken in the cone calorimeter and in the LOI, presented as a function of the metallic oxide content in the PVC compounds. A summary of DOE analysis results is also presented. Analysis was made via Minitab 15 software. This was made possible by the number of degrees of freedom available in measurements taken.

Figure 1 shows heat release curves versus time for the compounds, grouped according to the type of interaction between the metallic oxides studied in the formulation. Observing the curves in Figure 1 and the data in Table III for the peak heat release rate (PHRR) and the mean heat release rate (MHRR), it is possible to conclude that the presence of metallic oxides in the PVC compound formulation has a significant effect in this parameter. The ternary mixture, compared with the oxides used in isolation or in binary mixtures, is the one with the greatest reductions in both parameters when compared with the formulation taken as a reference. CuO and MoO$_3$, when isolated, give a better performance comparing with ZnO, and this is probably the reason for the better results given by the CuO/MoO$_3$ binary mixture when compared with the ternary mixture.

For the values of total heat released by the sample (THR, corresponding to the integration of the curves), the effects of metallic oxides on PVC compound formulation are also significant. The presence of metallic oxides significantly affects the samples' heat release profile; because, increasing quantities of metallic oxides shift the peak heat release rates to longer time periods, which is important from a material safety perspective in fire situations.[1,5–7,35]

MEHC values are affected significantly by the presence of metallic oxides. Because the MEHC value is determined in the cone calorimeter from gas phase data,[30] it can be concluded that the metallic oxides somehow affect the composition of gases that feed the combustion zone, making them energetically less rich, and in the end resulting in lower MHRR and THR values. Figure 2 shows carbon monoxide (CO) production rate curves versus time, for the formulations studied, according to the type of interaction between the metallic oxides studied in the formulation. Metallic oxides are seen to significantly alter the CO production rate, anticipating the emission peak rate, and intensifying it, especially in the case of the formulation to which ZnO was
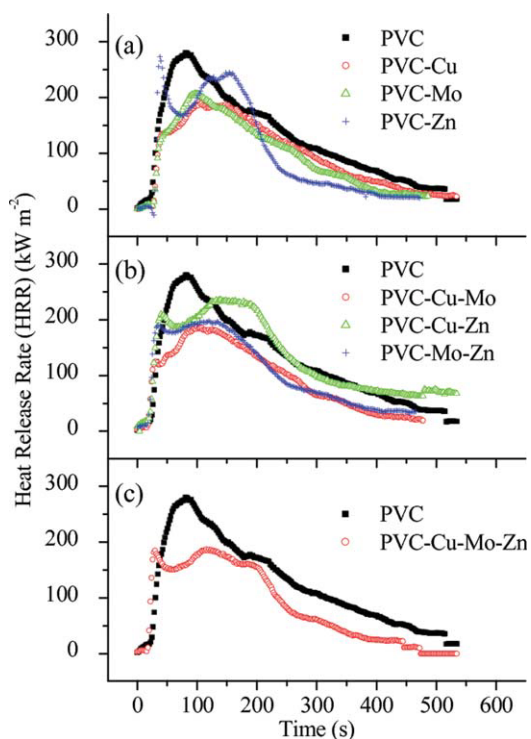
Figure 1 Heat release rate (HRR) curves for PVC/metallic oxides compounds, as a function of the interaction among metallic oxides, versus PVC reference composition: (a) single component effects; (b) binary interactions; (c) ternary interaction. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

added. This change in CO production behavior and the reduction in MEHC (except for the case of interaction between copper and zinc) is further evidence of change in the samples' combustion mechanism as a result of the compositional factors, leading to the belief that a less rich fuel and an incomplete combustion mechanism are introduced in the system.[33,34] The MEHC results obtained herein, despite statistical consistency and coherence with another study we recently published,[27] are the opposite of those obtained by Li and Wang[21,23–26] in studies using copper and molybdenum oxides incorporated into a rigid PVC compound. According to these authors, volatile substances of easier combustion are formed as a result of the presence of metallic oxides, which would explain the increase in MEHC values. However, the same cone calorimetric runs exhibited an increase in the CO production rate, but the authors do not comment on this observation.

Figure 3 shows smoke release rate curves versus time, for the compounds, according to the type of interaction between the metallic oxides studied in the formulation. The presence of metallic oxides is seen to have a very significant effect on smoke release of the PVC compounds. Observing Figure 3, it can be seen that the presence of metallic oxides in PVC compound formulation reduces the smoke

release rate, whereas promoting a delay in the peak rate, which is once again favorable for material safety in fire situations.[1,5–7,35]

The amount of carbonaceous residue left from the speciment at the end of the cone calorimeter measurement is another important parameter related to the release of smoke by materials during combustion, simply because one of the main mechanisms for reducing smoke is the fixation of organic matter in the solid phase, retarding/avoiding its pyrolysis and consequent combustion.[1,3,10–20] A simple check of Table III shows that all of the oxides studied have statistical significance in relation to char residue (CR) quantity values. To normalize the values for the diverse formulations studied, an additional column is shown in Table III corresponding to the normalized char residue (NCR) value for each formulation.[27] The NCR value was determined by multiplying the CR value, measured in the cone calorimetric assay by the mass fraction of reference PVC composite in each formulation as per data shown previously in Table II. Thus, all of the formulations can be compared based on the PVC composite's reference formulation. Analysis of the NCR results shows the effect of metallic oxides is significant, corroborating several studies conducted by
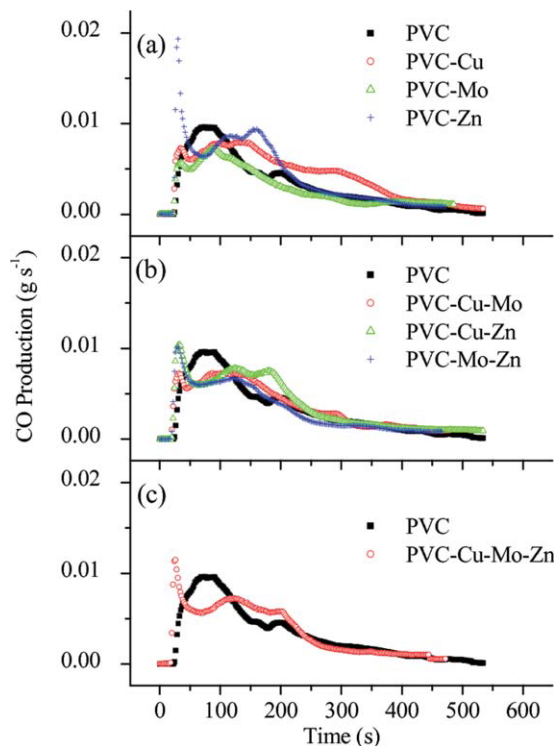

Figure 2 Carbon monoxide production curves for PVC/metallic oxides compounds, as a function of the interaction among metallic oxides, versus PVC reference composition: (a) single component effects; (b) binary interactions; (c) ternary interaction. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
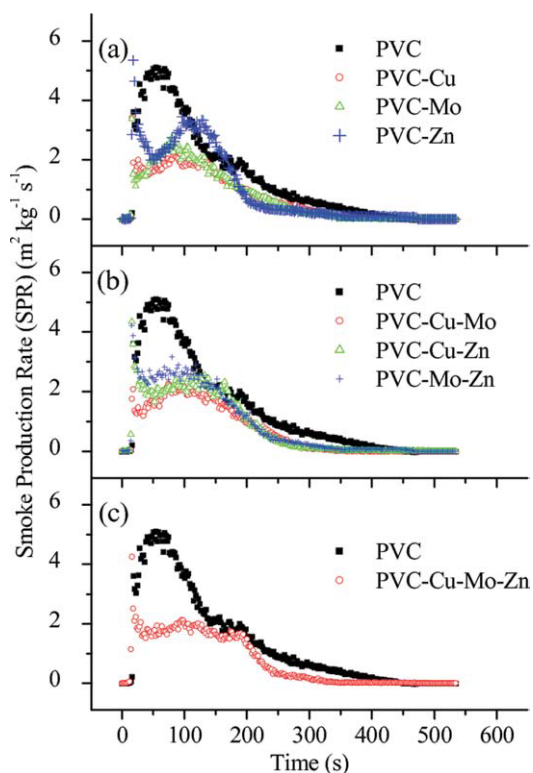
Figure 3 Smoke production rate (SPR) curves for PVC/metallic oxides compounds, as a function of the interaction among metallic oxides, versus PVC reference composition: (a) single component effects; (b) binary interactions; (c) ternary interaction. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Starnes Jr. and coworkers,[10–15] Kroenke and Lattimer[16–20] and Li and Wang,[21–26] confirming that the performance mechanisms of the main smoke suppressor agents used in PVC are based on interference in Diels-Alder condensation reactions and in the formation of benzene and other aromatic compounds. According to the authors, additives based on molybdenum interfere in the dechlorination process and in the formation of polyene sequences, anticipating their occurrence and forcing the formation of char, inducing the formation of structures fundamentally based on trans-polyens to the detriment of cis-polyens. Thus, the formation of benzene and other aromatic structures is reduced by the impossibility of carbon-carbon bond rotations. Thus, the preferential termination mode for the dehydrochlorination reaction becomes the Diels-Alder condensation, promoting the fixation of more carbon and hydrogen in the char and a more reduced tendency for soot and smoke formation. Likewise, copper and zinc based additives also accelerate dehydrochlorination reactions, increasing their rate. Copper, in particular, acts as an inductor agent in Diels-Alder condensation reactions through a reductive coupling mechanism, further favoring the fixation of carbon and hydrogen in the form of char, acting in

synergy with molybdenum composites. We also observed an elevated correlation between TSP and NCR values in another recently published study.[27]

Finally, LOI results show that the effects of metallic oxides are also statistically significant; in other words, the greater the content of these additives in the PVC compound formulation, the greater the difficulty in sustaining material combustion, denoted by the increase in LOI values.

Figure 4 shows the response surfaces obtained via Minitab software for the main cone calorimeter parameters: MHHR, THR, and TSP. The response surface for NCR is also shown for comparison and correlation purposes. The combination between CuO and MoO_3 proves to have the best balance among the different properties, permitting a reduction in the heat released during the combustion process and a reduction in the amount of smoke produced. In the formulations containing ZnO, perhaps as a result of the strong effect on the dehydrochlorination process, an increase in the amount of released heat, especially when in combination with CuO, and a worsening in smoke suppression performance can be observed, when compared to the other alternative studies.

Volumetric electrical resitivity

Table IV shows the results of volumetric electrical resistivity for the PVC compounds, according to the interaction between metallic oxides studied in the formulation. The presence of metallic oxides does not significantly affect the volumetric electrical resistivity of PVC compounds, studied here, as all the interactions have a statistical p-value > 0.05.

Dynamic thermal stability

Table IV also shows the results of dynamic thermal stability measurements for the PVC compounds, shown according to the interaction between metallic oxides studied in the formulation. The presence of metallic oxides is seen to have a very significant effect on the thermal stability of the PVC compound, reducing their value regardless of the type of metallic oxide in question, as denoted by the model's p-value. Here, once again, copper (II) and zinc oxide performance mechanisms stand out, as their performance principles in the case of smoke suppression are based on the acceleration of the PVC dehydrochlorination process.[13]

Thermogravimetry coupled to mass spectroscopy (TG/MS)

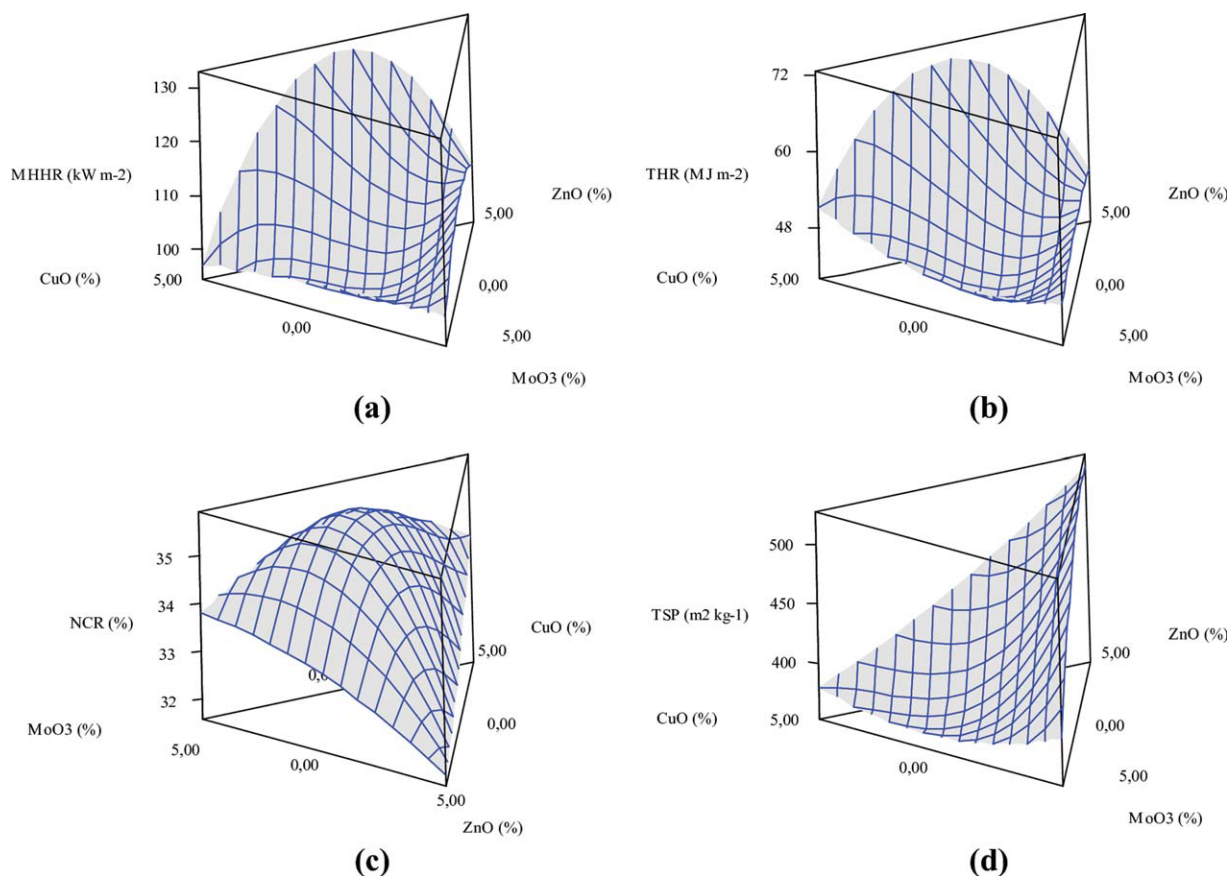Table V shows a summary of the main TG/MS measurement results, presented according to the type of

Figure 4 Surface response curves for PVC/metallic oxides compounds: (a) MHHR; (b) THR; (c) NCR; (d) TSP. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

interaction between metallic oxides studied in the formulation.

Figure 5 and 6 show the TG (Fig. 5) and the dTG (Fig. 6) curves for the PVC compounds, grouped according to the type of interaction between the metallic oxides studied in the formulation. In both curves and in the data shown in Table V, it is possible to observe that the presence of metallic oxides, regardless of their nature, accelerates the PVC compound dehydrochlorination process, promoting peaks of maximum decomposition rates at lower temperatures (T_{PDR}) and intensifying peak mass loss rates. Copper and molybdenum, in isolation or in a binary mixture, have a significant effect on T_{PDR}; however, zinc has the most pronounced effect even when in combination with the other metals, at these temperatures. The three types of oxides have a general effect on R_{PDR} value. The most pronounced effect occurs in situations where molybdenum is present, which is when the R_{PDR} value is highest. However, the R_{PDR} values for the ternary and MoO_3/ZnO mixtures are smaller than expected, considering the additive effect of each of the oxides incorporated. A more in-depth study of these effects must be conducted in the future for a better understanding.

These results once again corroborate the cone calorimeter observations and the dynamic thermal stability studies in the torque rheometer, as well as the diverse studies conducted by Starnes Jr. and coworkers,[10–15] Kroenke and Lattimer[16–20] and Li

TABLE IV
Volumetric Electrical Resistance (VER) and Dynamic Thermal Stability Results for PVC/Metallic Oxides Compounds

Formulation	VER (10^{13} Ohm cm)	Degradation onset (min)
PVC	2.63 ± 0.87	90.4 ± 3.0
PVC-Cu	1.37 ± 0.78	8.9 ± 0.2
PVC-Mo	3.14 ± 0.62	17.0 ± 0.8
PVC-Zn	3.10 ± 2.30	8.8 ± 0.1
PVC-Cu-Mo	2.58 ± 2.10	10.7 ± 0.6
PVC-Cu-Zn	2.69 ± 1.07	10.3 ± 0.2
PVC-Mo-Zn	3.37 ± 0.23	7.7 ± 0.4
PVC-Cu-Mo-Zn	2.50 ± 0.73	7.8 ± 0.6
Regression analysis (Minitab 15)		
Model (p-value)	0.488	0.000
Linear (p-value)	0.144	0.000
Binary (p-value)	0.934	0.000
Ternary (p-value)	0.574	0.011
Model R^2 (adjusted)	0.0000	0.9875

TABLE V
TG/MS Results for PVC/Metallic Oxides Compounds

Formulation	T_{ONSET} (°C)	T_{PDR} (°C)	R_{PDR} (% min^{-1})	Char Yield (%)	Area$_{HCl}$ ($\times 10^{-10}$ A min mg^{-1})	T_{HCl} (°C)	Area$_{C6H6}$ ($\times 10^{-12}$ A min mg^{-1})	T_{C6H6} (°C)
PVC	233.6	331.5	22.1	18.1	8.36	331.5	47.5	317.4
PVC-Cu	227.6	300.1	60.3	22.3	3.95	301.7	13.5	289.2
PVC-Mo	229.8	293.5	115.6	18.9	4.51	293.5	7.91	291.9
PVC-Zn	218.8	239.4	64.9	18.0	2.84	239.4	7.21	239.4
PVC-Cu-Mo	236.3	297.6	95.9	20.8	4.16	294.4	8.66	285.1
PVC-Cu-Zn	234.1	245.7	68.9	19.4	3.13	245.7	6.19	245.7
PVC-Mo-Zn	232.0	248.9	48.1	19.8	3.17	248.9	6.20	250.5
PVC-Cu-Mo-Zn	235.8	258.0	42.1	16.8	6.55	256.5	10.9	258.0

TG/MS parameters: T_{ONSET} – Temperature of the onset of dehydrochlorination (TG); T_{PDR} – Temperature at peak decomposition rate (dTG); R_{PDR} – Rate of mass loss at peak decomposition rate (dTG); Area$_{HCl}$ – Integration result of the curve QMID HCl × Temperature; T_{HCl} – Peak temperature of the curve QMID HCl × Temperature; Area$_{C6H6}$ – Integration result of the curve QMID C$_6$H$_6$ × Temperature; T_{C6H6} – Peak temperature of the curve QMID C$_6$H$_6$ × Temperature.

and Wang,[21–26] demonstrating the anticipation and acceleration effect of processes tied to dehydrochlorination.

The use of the MS-TG coupling technique reveals important data about sample degradation mechanisms. Figures 7 and 8 show the detection rate curves in MS for HCl (Fig. 7) and benzene (Fig. 8) for the PVC compounds, grouped according to the type of interaction between the metallic oxides stud-

ied in the formulation. As observed for TG, acceleration in the dehydrochlorination process is verified, because the HCl release rate peaks occur at lower temperatures, with the intensities relatively maintained among the different formulations. Once again, ZnO has a more pronounced anticipation than the other metallic oxides, when it is present in isolation as well as in binary and ternary mixtures. A strong and significant reduction in the formation of
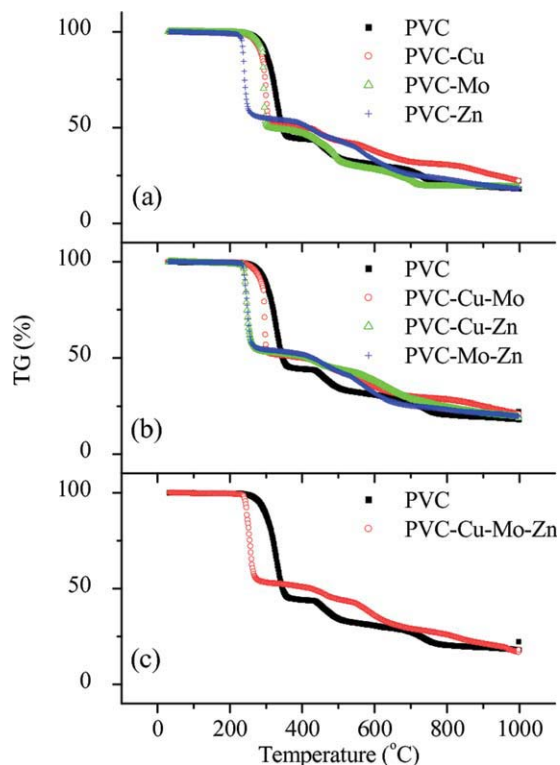

Figure 5 TG curves for PVC/metallic oxides compounds, as a function of the interaction among metallic oxides, versus PVC reference composition: (a) single component effects; (b) binary interactions; (c) ternary interaction. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
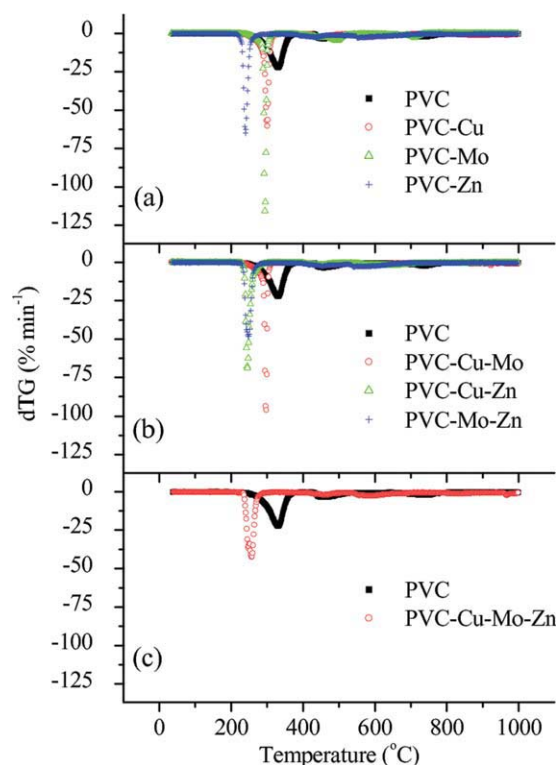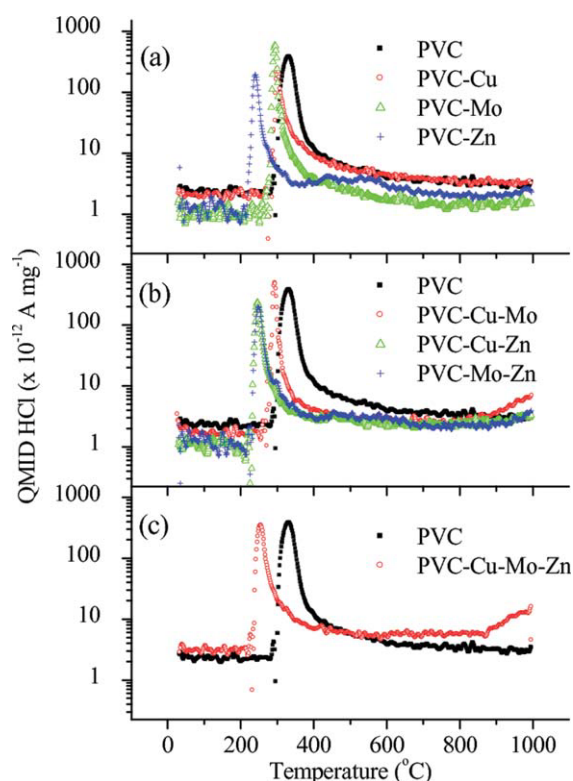

Figure 6 dTG curves for PVC/metallic oxides compounds, as a function of the interaction among metallic oxides, versus PVC reference composition: (a) single component effects; (b) binary interactions; (c) ternary interaction. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Figure 7 Mass spectroscopy curves for HCl released during the pirolysis of PVC/metallic oxides compounds, as a function of the interaction among metallic oxides, versus PVC reference composition: (a) single component effects; (b) binary interactions; (c) ternary interaction. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

benzene can be observed qualitatively in Figure 8, and quantitatively from the integration data of detection rate curves for benzene versus time, shown in Table V, because of the presence of metallic oxides in the formulations, which once again confirms and demonstrates the mechanisms proposed by Starnes Jr. and coworkers,[10–15] Kroenke and Lattimer[16–20] and Li and Wang.[21–26]

Scanning electron microscopy (SEM)

Figure 9 shows the SEM observation results for the ashes resulting from the PVC compounds pyrolysis process, grouped according to the type of interaction between metallic oxides studied in the formulation. Different char morphologies are observed as a result of the composition of the formulation. Especially in those cases where CuO is present, the superficial layer of char is clearly fractured, whereas in the cases where the incorporated oxide was MoO_3 and/or ZnO the structure of the superficial layer apparently remains preserved after the pyrolysis process. These structural alterations normally correlate to the peak heat release or mass loss rates in the cone calo-

rimeter.[33,34] However, in this case, it was not possible to observe any sort of correlation, perhaps because the pyrolysis temperature used to generate the samples for SEM/EDS observation was too low when compared with the actual temperature reached during combustion in the cone calorimeter. Examination of EDS traces, resulting from SEM observations, shows that the three metals studied, apparently, act on the combustion process and smoke emission in the solid phase, because all atomic species are detected by EDS in the ashes resulting from the combustion process. However, a similar study that we recently published[27] showed that, the zinc metal was not detected in the PVC/metallic oxides/O-MMT ashes. This raised the hypothesis that its effect, at least in the combustion process, could occur in the gas phase, or that zinc, probably in the form of zinc oxychloride, could vaporize during the pyrolysis cycle in the muffle furnace. New studies of the reaction's composition and kinetics in the gas phase need to be conducted in the future to confirm these hypotheses.
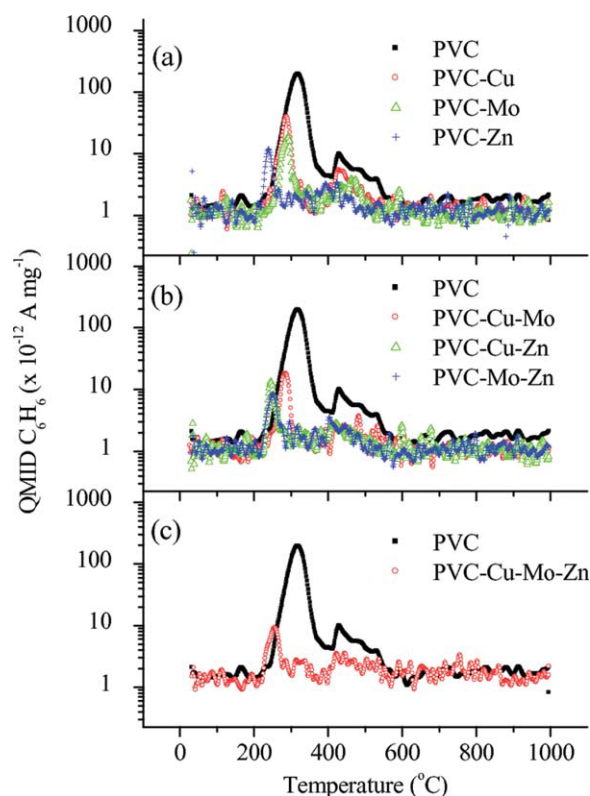

Figure 8 Mass spectroscopy curves for benzene released during the pirolysis of PVC/metallic oxides compounds, as a function of the interaction among metallic oxides, versus PVC reference composition: (a) single component effects; (b) binary interactions; (c) ternary interaction. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
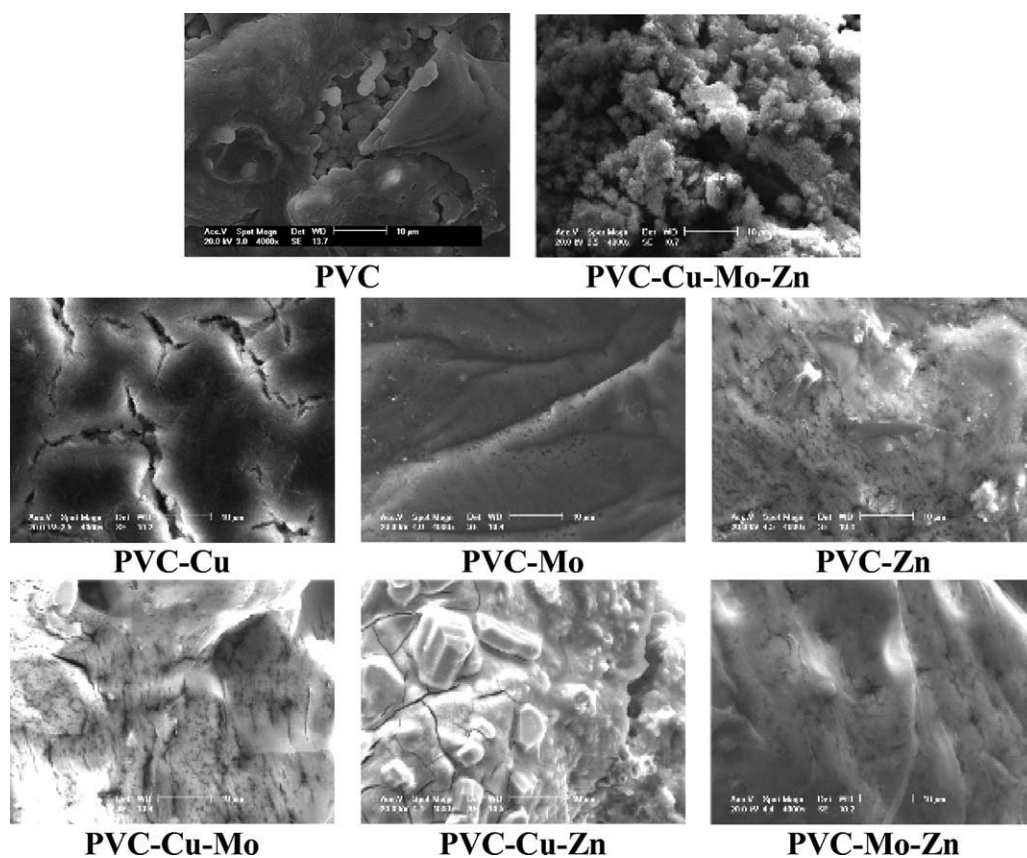
Figure 9 SEM images for PVC/metallic oxides compounds. Reference bars = 10 microns.

CONCLUSIONS

Cone calorimeter measurements conducted on PVC compounds modified with different copper (II), molybdenum and zinc oxide mixtures, at a radiant heat flux of 50 kW m^{-2}, revealed that these oxides have a very significant effect on combustion properties and smoke suppression, especially in the most important ones for safety requirements in fire situations. The presence of metallic oxides in the formulation of PVC compounds was observed to retard heat release and smoke emissions of studied samples and to reduce their absolute quantities.

Cone calorimeter measurements offer strong indications that metallic oxides significantly affect the combustion mechanisms of the PVC compounds. They affect both the mean effective heat of combustion (MEHC) and the amount of released carbon monoxide values, indicating the occurrence of a less efficient combustion process, possibly resulting from the generation of a less rich fuel and/or incomplete combustion mechanisms introduced in the system. This study did not reveal whether these effects result from mechanisms introduced in the solid phase and/or the gas phase; however, the presence of the metals in ashes studied by SEM/ EDS indicate the need for a more in-depth analysis of this topic.

Result obtained also confirm the mechanisms proposed by Starnes Jr. and coworkers, Kroenke and Lattimer, and Li and Wang, that is, the anticipation of dehydrochlorination reactions, reductive coupling and benzene suppression resulting from the presence of copper, molybdenum and zinc metals. These phenomena could be observed in the TG/dTG results, the increase in postcombustion char residue in the cone calorimeter measurements, and in the significant reduction in benzene production, in the latter case, indicated in the MS measurements taken.

The results also indicate that the combination of copper and molybdenum oxides provides the best balance of combustion properties, because it reduces the amount of heat released and promotes the most efficient smoke suppression. Formulations containing ZnO, because of its strong Lewis acid characteristic, indicate a less pronounced reduction of smoke released during the combustion process, when compared with copper (II) and molybdenum oxides.

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