STUDY OF FLAMMABILITY CHARACTERISTICS OF POLY(VINYL CHLORIDE)

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Abstract. The polymer materials are being used in several applications. In buildings, the rigid poly(vinyl chloride) is extensively used since it has self-extinguishable character and is able to be mixed with a lot of additives and then result in materials with different mechanical, thermal and flammability characteristics. However, besides the recognized self-extinguishable behavior, the poly(vinyl chloride) releases smoke in burning conditions. Considering that the use of these materials has increased, the study of their flammability characteristics becames important for the industries and the scientific community. The aim of this work is to study the flammability properties of the rigid PVC materials. Vertical and horizontal burning, limit oxygen index, flash ignition temperature, self-ignition temperature and density of smoke tests were performed. The good flammability properties of PVC were observed in vertical and horizontal burning tests, and the materials didn't allowed the flame propagation. For the tests of limit oxygen index (LOI), self-ignition and flash ignition temperature and smoke density, the materials with flame retardant or smoke supressant showed improvements on the properties. The PVC 3, with flame retardant and smoke supressant presented the best results in LOI and index of smoke releasing tests.

Keywords: flammability, poly(vinyl chloride)

1. INTRODUCTION

PVC is compatible with a wide range of additives, and its behavior can be modified to suit many market requirements at reasonable cost. Many of the organic additives are flammable and affect the fire resistance of formulated PVC. The largest volume uses for rigid PVC include pipe and fittings, window profiles, custom moldings such as computer housings and electrical junction boxes, outdoor products such as decking, and thermoformed parts and containers (Coaker, 2003).

The burning of polymers involves several steps, beginning with the cleavage of chemical bonds to give molecules with some volatility and their escape into the vapor phase. Further degradation of these species then occurs to give small radicals which actually make up the flame. Finally, the feedback of energy from the flame to the surface of the polymer continues the process. Fire retardants may function by interfering with any of these three steps (Wilkie, 1999).

Polyvinyl chloride does not exist as the pure substance other than at a polymerization site. Neat PVC, i.e., rigid or unplasticized PVC, is difficult to ignite, and will cease burning as soon as the source of heat or flame is removed. Neat PVC has 56.8 % chlorine content and an oxygen index about 47 %, compared to most non-halogen polymers, which have oxygen indices ranging from 17.4 % (polypropylene or polymethyl methacrylate) to 26 % (polycarbonate). Because of its high content of chlorine, which is a non-contributor to the heat of combustion, the heat release characteristic of unplasticized PVC is the lowest of all commodity plastics. However, the smoke developed index of rigid PVC tends to be poor, unless smoke suppressant additives are used (Weil *et al.*, 2006).

This study will characterize the flammability properties of different PVC formulations containing flame retardant (Sb_2O_3) , smoke suppressant (molybdenum compound) and a formulation with both additives.

1.1 Flame Retardant

Antimony oxide (antimony trioxide, Sb_2O_3), although usually not effective as a flame retardant in the absence of halogen, is a powerful synergist in halogenated polymers such as PVC. It is typically used in the range of 3–7 phr (rarely as much as 12 phr). The use of antimony oxide in PVC generally elevates the smoke level relative to the mass burned in small-scale tests, but on the other hand, the total smoke may be lowered in a large-scale test or in an actual fire because of the reduction in the amount or rate of polymer burning (Weil *et al.*, 2006).

1.2 Supressant additive

Molybdenum compounds are regarded as the standard additives for low-smoke formulations, the leading additive being ammonium octamolybdate (AOM) for vinyl applications. Studies have shown that molybdates work in the solid phase as most of the molybdenum is found in the char residue (Weil *et al.*, 2006).

2. EXPERIMETAL SECTION

The tab. 1 shows the PVC formulations, and tab. 2 gives the samples' dimensions used for tests.

	PVC - standard	PVC 1	PVC – 2	PVC – 3	Observations
PVC resin	100	100	100	100	
Thermal stabilizing	3	3	3	3	
CaCO ₃	15	15	15	15	
TiO ₂	2,5	2,5	2,5	2,5	White pigment
SbO ₃	0	5	0	2,5	Flame retardant
Charmax LS100	0	0	5	2,5	Smoke suppressant

Table 1. Formulations in phr (parts in each a hundred parts of resin).

Table 2.	Samples'	dimensions.

Test	Dimensions (mm)	Mass (g)	
Vertical burning	125 x 13 x 3	Not applicable	
Horizontal burning	125 x 13 x 3	Not applicable	
LOI	125 x 13 x 3	Not applicable	
Flash ignition temperature	20 x 20 x 3	Enough for sample ignition	
Self-ignition temperature	20 x 20 x 3	Enough for sample ignition	
Smoke density	25 x 25 x 3	3 to 4 g	

2.1 Vertical Burning

The test was performed according to ASTM D3801. The burner remote was adjusted to produce a blue flame 20 mm high. The ignition source was placed centrally under the lower end of the test specimen. It was recorded the total flaming time (the length of time for which a material continues to flame, after the ignition source has been removed).

2.2 Horizontal Burning

The horizontal burning of samples was done according to ASTM D635. Specimens were marked with two lines perpendicular to the longitudinal axis of the bar, 25 and 100 mm from the end that would be ignited. The burner remote was adjusted to produce a blue flame 20 mm high. The ignition source was applied and the time of flame and the burning extension were observed.

2.3 Limit Oxygen Index

A mixture of commercial nitrogen and oxygen gases was used. The guide for this test was the ASTM D2863. The gas velocity through the glass tube was 40 mm/s. It was set an initial oxygen concentration. The burner was adjusted and the visible flame was applied to the end face of the specimen and also, to a depth of approximately 6 mm. If neither the period nor extent of burning exceeded the relevant limit specified in ASTM D2863 for the applicable specimen, the oxygen concentration was increased.

2.4 Flash ignition temperature and self-ignition temperature

The flash ignition and self-ignition temperature tests were performed using an oven with hot air. The proceedings were followed according to the ASTM D1929. An electrical current of 20 A (responsible for the heating index) and an air flow of 5 L/min (responsible for oxygen supply) were used. The air temperature inside de oven and the sample temperature were recorded until the flash ignition or self-ignition temperatures were reached. For the flash ignition temperature test, an ignition source was used.

2.5 Smoke density

This test was done according to the ASTM D 2843. Three tests were performed for each kind of material, and the results are the average of these. Considering that the mass and the geometry of the samples are extremely important for the test, the samples were carefully cut.

The sample was placed on the support and the flame was adjusted to be positioned directly under the sample. It was recorded the percent light absorbed at 15-s intervals for 4 minutes.

3. RESULTS AND DISCUSSION

3.1 Vertical and horizontal burning

All the formulations tested showed the same extinguishable behavior. For vertical burning tests, the flame was applied twice during 10 s, and after flame was removed, the fire propagation ceased.

During the horizontal burning tests, the flame was applied once for 30 s, and fire propagation ceased immediately after that.

This PVC behavior was previously expected for vertical and horizontal burning tests. According to Weil *et al.* (2006), rigid or unplasticized PVC is difficult to ignite, and will cease burning as soon as the source of heat or flame is removed.

3.2 Limit oxygen index

Coaker (2003) showed the limit oxygen index (LOI) of some thermoplastics. According to him, it is clear that PVC has a big advantage over ABS, PS, and polyolefins in this property. Also, the author affirms that, starting from a higher initial LOI, PVC is easier to flame retard than many other thermoplastics. The advantage is increased because the chlorine in PVC works synergistically with many flame retardants. The studies show a LOI of 45-49 % for rigid PVC and a LOI of 60-70 % for chlorinated PVC.

In this work, the standard PVC showed a LOI of 52 %. The others formulations showed higher LOI numbers than the standard. These results suggest the improvement of flammability properties by flame retardant and smoke suppressant additives.

The fig. 1 shows the results obtained on LOI tests.

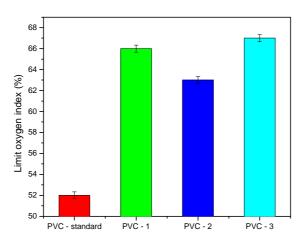


Figure 1. Limit oxygen index.

3.3 Flash Ignition Temperature

For this test, samples with flame retardant and samples with smoke suppressant showed similar results. Also, the flash ignition temperatures for these materials were not much higher than the standard material. The higher result was observed for PVC 3, the material with both additives.

The studies of Gallo and Agnelli (1998) show a flash ignition temperature for PVC of 390 °C. This study showed a flash ignition temperature, for neat PVC (without flame retardant or smoke suppressant), higher than the literature result.

Figure 2 shows the flash ignition temperatures for PVC formulations.

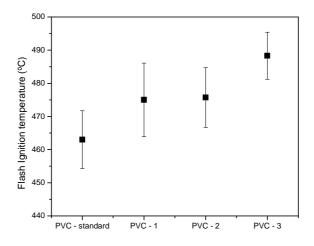


Figure 2. Flash Ignition temperature.

3.4 Self-ignition temperature

The samples with flame retardant or with smoke suppressant showed self-ignition temperatures much higher than the standard material. However, the PVC 3 presented almost the same behavior of standard PVC.

Gallo and Agnelli (1998) cited the self-ignition temperature for some polymer materials, and in their review the temperature for PVC is 450 °C. Therefore, the present study shows that the standard formulation had a similar behavior of Gallo and Agnelli (1998). Formulations with additives had improvements in this property.

Figure 3 illustrates the results of the self-ignition temperature test.

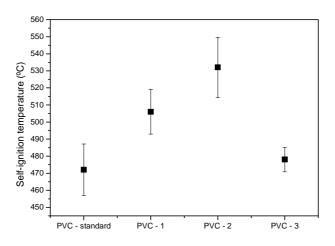


Figure 3. Self-ignition temperature.

3.4 Smoke density

The index of smoke releasing was calculated by the graphics of light absorption. For this test, the PVC 1 and 2 showed lower index of smoke than the standard material. PVC 3 presented the lowest result for this test.

According to Innes and Cox (1997) studies, there are a number of smoke suppressants available. They are frequently based on molybdenum or zinc compounds and it has been demonstrated that molybdenum acts as a flame/smoke suppressant in the solid phase. It has also been shown that the difference between the vapor phase action of antimony oxide, Sb_2O_3 , and the solid state action of molybdenum is based on their reactivity with halogen acid gas. Antimony oxide reacts with hydrogen chloride, HCl, at room temperature and this antimony chloride vaporizes at below 100 °C while molybdenum oxide reacts but does not vaporize below 265 °C.

The possibility of different actions of flame retardant and smoke suppressant in PVC formulations can be cited as an important reason for the positive result of index of smoke releasing. Also, it can explain the positive synergetic action to improve the index of smoke releasing for the PVC 3.

Figures 4 and 5 illustrate the average of light absorption for materials. The fig. 6 shows index of smoke releasing.

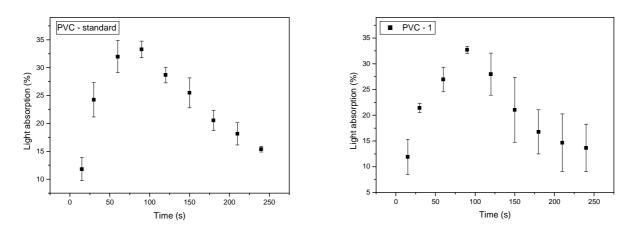


Figure 4. Light absorption for PVC standard and for PVC 1.

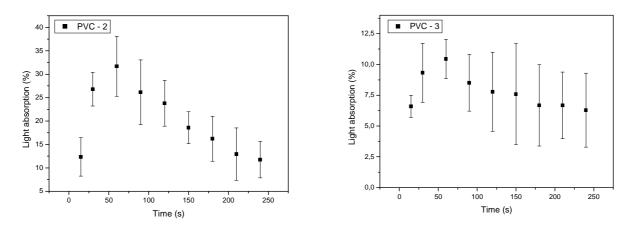


Figure 5. Light absorption for PVC 2 and for PVC 3.

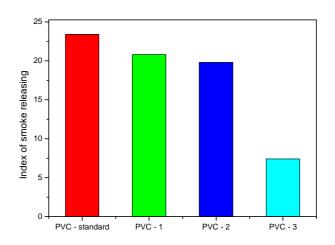


Figure 6. Index of smoke releasing.

4. CONCLUSIONS

On the vertical and horizontal burning tests, the flame was extinguished immediately after ignition source was removed, what means that all formulations showed self-extinguishable character. Although these tests prove the good flammability properties of poly(vinyl chloride), they were not useful to differentiate the rigid PVC materials.

The PVC formulations containing flame retardant and smoke suppressant showed, when compared with standard material, higher LOI, higher flash ignition temperature and higher self-ignition temperature. Also, the PVC with additives presented lower indices of smoke releasing.

The PVC 3 presented the highest LOI, and the smoke developed index was lower than to the other formulations.

Analyzing the different tests performed, it's possible to affirm that the addition of flame retardant and smoke suppressant in rigid PVC shows a positive synergetic action to improve the materials' flammability properties.

5. ACKNOWLEDGEMENTS

To Capes, for the scholarship.

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6. REFERENCES

American Society for Testing Materials ASTM 2843 Density of Smoke from the Burning or Decomposition of Plastics.

American Society for Testing Materials ASTM 2863 Measuring the Minimum Oxygen Concentration to Support Candle-Like Combustion of Plastics (Oxygen Index).

American Society for Testing Materials ASTM 3801 Measuring the Comparative Burning Characteristics of Solid Plastics in a Vertical Position.

American Society for Testing Materials ASTM 635 Rate of Burning and/or Extent and Time of Burning of Plastics in a Horizontal Position.

American Society for Testing Materials ASTM D 1929 Standard Test Method for Determining Ignition Temperature of Plastics.

Coaker, A. W., 2003, "Fire and Flame Retardants for PVC", J. of Vinyl & Additive Technology, vol. 9, no. 3, pp. 108-115.

Gallo, J. B., Agnelli, J. A. M., 1997, "Aspectos de Comportamento de Polímeros em Condições de Incêndio", Polímeros: Ciência e Tecnologia, no.1, pp. 23-37

Innes, J. D. and Cox, A. W., 1997, "Smoke: Test Standards, Mechanisms, Suppressants", J. of Fire Sciences, vol. 15, pp. 227-239.

Weil, E. D. *et al.*, 2006, "Flame and Smoke Retardants in Vinyl Chloride Polymers – Commercial Usage and Current Developments", J. of Fire Sciences, vol. 24, pp. 211-236.

Wilkie, C. A., 1999, "Adventures in Fire Retardancy", J. of Vinyl & Additive Technology, Vol. 5, No. 4, pp. 172-185.

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