

Studies on the Effects of Ammonium Phosphates on the Flammability Properties of Poly(Vinyl Alcohol) Films

*¹H. Abba, ²H. Musa, ³A.A. Kogo and ²A.A. Salisu

¹Department of Chemistry, Ahmadu Bello University, Zaria, Nigeria.

²Department of Pure and Industrial Chemistry, Bayero University, Kano, Nigeria.

³Department of Textile Science and Technology, Ahmadu Bello University, Zaria.

[*Correspondence Author's e-mail: habba@abu.edu.ng, hamzaabbah@yahoo.com; ☎: +2348028333784]

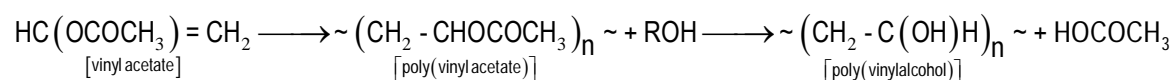
ABSTRACT: Poly(vinyl alcohol) was solvent-cast from aqueous solution of n-hexane into 125 μm films. Three ammonium phosphates, (NH₄)₃PO₄, NH₄H₂PO₄ and (NH₄)₂HPO₄, were then added to produce eight sample films. Burning time, flame spread, limiting oxygen index, ignition time, and after-glow time of the samples were evaluated to determine the flame retardant efficiency of the three fillers. From the results, burning time, flame spread, after-glow time, and ignition response indices of the filled samples were found to be lower than the control sample. However, limiting oxygen index of the filled samples was found to be higher than that of the control sample. The efficiency of the fillers in fireproofing the poly(vinyl alcohol) film was found to follow the order (NH₄)₃PO₄ > NH₄H₂PO₄ > (NH₄)₂HPO₄. Additive effect was observed when the fillers are added in pairs with the fireproofing efficiency following the order (NH₄)₃PO₄ + NH₄H₂PO₄ > (NH₄)₃PO₄ + (NH₄)₂HPO₄ > (NH₄)₂HPO₄ + NH₄H₂PO₄. Antagonism in fireproofing efficiency was observed when all the three fillers were present in the poly(vinyl alcohol) film. The fireproofing efficiency of the ammonium salts is attributed to the quantity and the ease with which ammonia (NH₃) gas is released when the filled poly(vinyl alcohol) films were heated.

Keywords: Ammonia, fireproof, flammability, ignition, plastic film

INTRODUCTION

Synthetic polymers have revolutionized the way we live since their discovery about a century ago and their wide-scale availability in the last 60 years. Through their specific features – versatility, convenience and economics, they now make up, or are essential components of most of the articles we depend on in our everyday lives (McCrum *et al*, 1997 and Dara, 2007). Synthetic polymers, especially plastics, are increasingly usurping many functions of the materials traditionally used by man; metals, glass, wood, ceramics, etc (Rudin, 2006). The technology of

applications of polymers has become more advanced with the use of additives, such as flame retardants. Most plastics contain additives incorporated into their formulations to modify some properties that allow them to effectively fulfill their intended use (Baer 1996 and Mihai *et al*, 2007). Although poly(vinyl acetate) can be converted to poly(vinyl alcohol) by aminolysis, hydrolysis, or trans-esterification, industrially, the most important reaction is that of trans-esterification where an acid or a base is added in catalytic amounts to promote the ester inter-change (Brown *et al*, 2005):



Poly(vinyl alcohol) is linear with side chains of secondary alcohol groups and is a versatile polymer with many industrial applications. The long established uses of poly(vinyl alcohol) continue to be of technical and economic significance as developments in the last four decades have shown (Painter and Coleman, 1999).

Flammability of materials is an important parameter that has been, and still is, an active area of research (Armstrong, 2005). Poly(vinyl alcohol) burns like paper (Varatharajan and Williams, 2000) and, consequently, flame retardants are essential to protect its products against direct flaming (Rubinstein and Colby, 2006). In this study, three ammonium phosphates, (NH₄)₃PO₄, (NH₄)₂HPO₄, and NH₄H₂PO₄, were incorporated into

poly(vinyl alcohol), singly and in combination, to study their effects on flammability properties in comparison to a control sample.

MATERIALS AND METHODS

Poly(vinyl alcohol) (Rhodoviol) powder and n-hexane were obtained from Rhone-Poulenc, France, and the three ammonium phosphates ((NH₄)₃PO₄, (NH₄)₂HPO₄, and NH₄H₂PO₄) used in formulating the films were all analytical-reagent grade obtained from Hoechst Chemicals AG, Frankfurt, Germany.

Sample Preparation

125 µm-thick film of pure (additive-free) Rhodoviol was prepared using n-hexane as solvent by the casting technique into a 12.20 X 1.22 X 0.13 cm mould (Sample A). This procedure was repeated by adding 7.5 % w/w of the three fillers ((NH₄)₃PO₄, (NH₄)₂HPO₄, and NH₄H₂PO₄), singly, in pairs and all the three fillers combined, to the pure Rhodoviol powder i.e.:

- A = Pure poly(vinyl alcohol) as control
- B = poly(vinyl alcohol) + (NH₄)₃PO₄
- C = poly(vinyl alcohol) + (NH₄)₂HPO₄
- D = poly(vinyl alcohol) + NH₄H₂PO₄
- E = poly(vinyl alcohol) + (NH₄)₃PO₄ + (NH₄)₂HPO₄
- F = poly(vinyl alcohol) + (NH₄)₃PO₄ + NH₄H₂PO₄
- G = poly(vinyl alcohol) + (NH₄)₂HPO₄ + NH₄H₂PO₄
- H = poly(vinyl alcohol) + (NH₄)₃PO₄ + (NH₄)₂HPO₄ + NH₄H₂PO₄ sample.

Burning Time

A Bunsen-burner flame was applied to the bottom of each sample in a vertical position and the time taken for the sample to burn to the 7.5 cm mark was noted according to ASTM D 568 (Angel and Reid, 2006; Anon, 2008). The procedure was repeated three times and the average value reported as each sample's burning time.

Flame Spread

Each sample was supported on a 45-Degree Incline and ignited with a flame from a hypodermic needle and burning allowed on both sides of each sample. The time taken for the burning-through of each sample was noted according to ASTM D 1433 (Sperling, 2006; Anon, 2008). The procedure was repeated three times and the average value reported as flame spread.

Limiting Oxygen Index (LOI)

Each sample was mounted vertically and ignited at the top with a Bunsen-burner flame. The

concentration of oxygen in the atmosphere flowing past each sample was lowered to the minimum and the amount that supports combustion for each sample noted according to ASTM D 2863 (Anon, 2008; Davis, 2008). The procedure was repeated three times and the average value reported as LOI.

Ignition Time/Ignition Response Index (IRI)

A Bunsen-burner flame was applied to the lower edge of each sample in a vertical position and the time of flame impingement that causes each sample to ignite was recorded according to ASTM D 3713 (Allcock *et al.*, 2003 and Anon, 2008). The procedure was repeated three times and the average value reported as each sample's response to flame impingement (ignition time).

After-Glow Time

A Bunsen-burner flame was applied to the lower edge of each sample in a vertical position. The flame was removed and the time taken for the burning sample to extinguish noted according to ASTM D 3801 (Rattan, 2007 and Anon, 2008). The procedure was repeated three times and the average value reported as the after-glow time.

RESULTS AND DISCUSSION

The results of the study are shown in Figure 1 and Table 1. Figure 1 shows the burning time, flame spread and after-glow time of the eight sample films used in the study. From the Figure, it can be seen that all the three ammonium phosphate fillers are capable of inducing self-extinguishing property in poly(vinyl alcohol) in the amount of the fillers added (7.5 % w/w). Comparing the burning times of the filled sample films, the film containing all the three fillers has the longest burning time of 52 seconds. It is second only to the control sample (A), which has a burning time of 57 seconds. The burning times of the sample films singly filled with the three ammonium salts (samples B, C and D) are higher than those samples containing pairs of the three ammonium salts (samples E, F and G). The susceptibility of the samples to burning follows the order F > E > G > B > D > C > H > A. It can also be observed that the presence of the fillers decreases the time taken for the 7.5 cm sample films to burn.

Similar trends of susceptibility of the samples to both flame spread and after-glow time can be observed. These results imply that, although to varying extents, all the three ammonium salts (singly and/or in combination) have reduced the burning time of the pure poly(vinyl alcohol) polymer.

Table 1 presents the results of the limiting oxygen index and the ignition index of the sample films. From the Table, It can be seen that the LOI of the control sample (A) is only 18.75. It can also be observed that the filled samples have higher limiting oxygen indices, although to different degrees, than the control sample. This implies that the filled samples need larger amount of oxygen to burn than the control sample. The order of limiting oxygen index (LOI) can be seen to follow the order: A < H < C < D < B < G < E < F. The LOI values of all the samples further indicate that only samples A and H are flammable, as their LOI values < 21. This is, as reported earlier, due to the fact that any material whose LOI value ≤ 21 is considered flammable (Hwan-Man *et al*, 2003). The values of ignition times of the samples, from Table 1, can be seen to follow an opposite trend to that of LOI,

with the order of ignition time being F < E < G < B < D < C < H < A.

The results obtained can be ascribed to the products of the equations for the burning of the three ammonium phosphates shown in Scheme 1. Ammonium phosphates thermally decompose into tetraoxophosphate (V) acid (H_3PO_4) and ammonia (NH_3). The ammonia produced is reported to act as a strong base in the condensed phases (solid and liquid) and as a diluent in the gaseous phase (Allcock *et al*, 2003). Since ammonia does not support combustion, it shields the poly(vinyl alcohol) films from being accessed by air, slows the flame propagation, narrows the flammability limits and cools the already burning material.

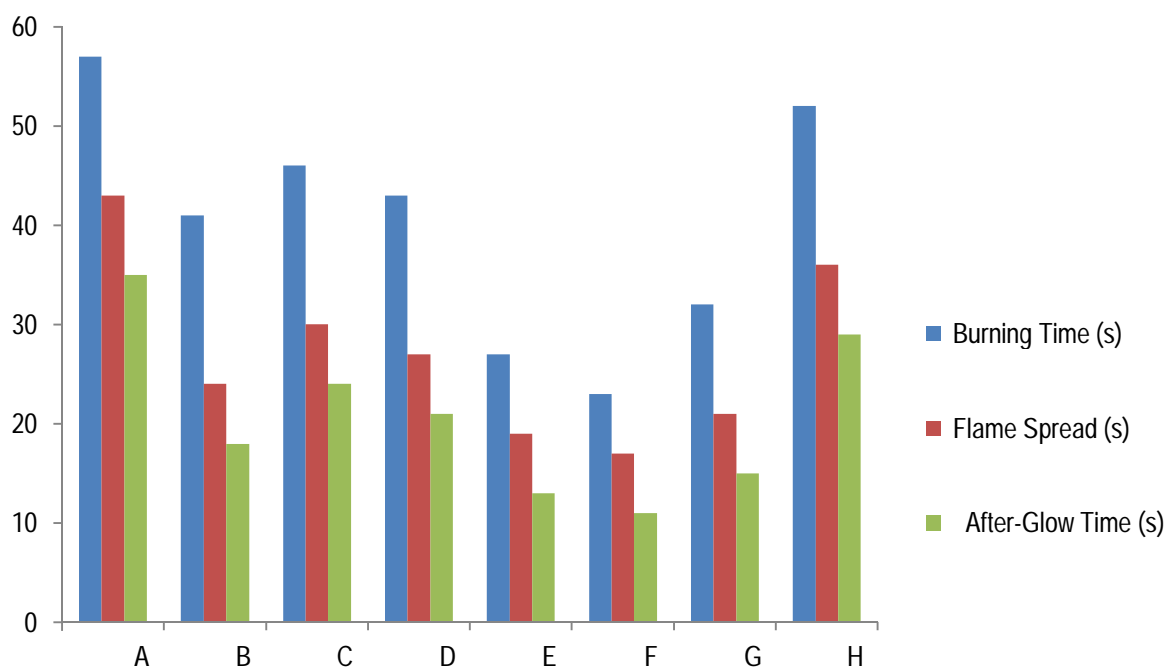
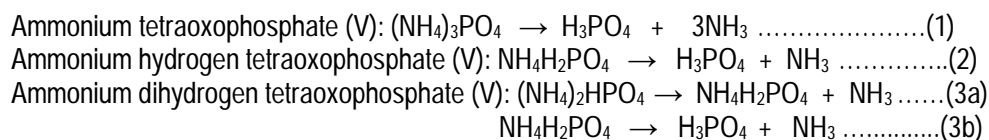


Figure 1: The burning time, flame spread and after-glow time of the eight poly(vinyl alcohol) sample films

Table 1: The limiting oxygen index (LOI) and Ignition Time/Ignition Response Index (IRI) of the eight poly(vinyl alcohol) sample films.

Sample Code	LOI	Ignition Time (s)
A	18.75	32
B	38.97	15
C	31.57	21
D	35.64	18
E	46.12	11
F	51.05	9
G	41.23	12
H	19.35	26



Scheme 1: Equations for the combustion of the three ammonium phosphates used in filling the poly(vinyl alcohol) films.

From Scheme 1, it can be observed that the order of efficiency of the ammonium phosphate salts is $(\text{NH}_4)_3\text{PO}_4 > \text{NH}_4\text{H}_2\text{PO}_4 > (\text{NH}_4)_2\text{HPO}_4$. This is because, as can be seen from equation 1, that $(\text{NH}_4)_3\text{PO}_4$ decomposes to yield three molecules of ammonia (NH_3). It is followed, as can be seen from equation 2, by $\text{NH}_4\text{H}_2\text{PO}_4$, which decomposes to yield one molecule of ammonia (NH_3). That $\text{NH}_4\text{H}_2\text{PO}_4$ is more efficient than $(\text{NH}_4)_2\text{HPO}_4$ can be seen from equations 3a and 3b. Although ammonia (NH_3) is produced in equation 3a, this is in addition to $\text{NH}_4\text{H}_2\text{PO}_4$, without the formation of H_3PO_4 . It is only if $\text{NH}_4\text{H}_2\text{PO}_4$ decomposes, in equation 3b, that H_3PO_4 is produced.

The overall fireproofing efficiency of the eight sample films are in the order: $(\text{NH}_4)_3\text{PO}_4 + \text{NH}_4\text{H}_2\text{PO}_4 > (\text{NH}_4)_3\text{PO}_4 + (\text{NH}_4)_2\text{HPO}_4 > (\text{NH}_4)_2\text{HPO}_4 + \text{NH}_4\text{H}_2\text{PO}_4 > (\text{NH}_4)_3\text{PO}_4 > \text{NH}_4\text{H}_2\text{PO}_4 > (\text{NH}_4)_2\text{HPO}_4 > (\text{NH}_4)_3\text{PO}_4 + (\text{NH}_4)_2\text{HPO}_4 + \text{NH}_4\text{H}_2\text{PO}_4 > \text{pure/unfilled/control poly(vinyl alcohol)}$.

CONCLUSION

The results of this study have shown that all the three ammonium salts, singly and combined, markedly improve the flame retarding efficiency of the poly(vinyl alcohol) plastic film. Consequently, their use in preventing ignition and/or spread of flame, in place of the very expensive oxides of antimony, bismuth and molybdenum and toxic halogenated hydrocarbons, in the formulations of fireproofing poly(vinyl alcohol) films is strongly recommended.

REFERENCES

Allcock, H.R., Lampe, F.W. and Mark, J. E. (2003). *Contemporary Polymer Chemistry*, 3rd edn, Pearson Education, New York, Pp.213-137.
 Angel, T. and Reid, P. (2006). *Physical Chemistry*, Benjamin Cummings, San Francisco, Pp.869-871.

Anonymous (2008). *Annual Book of ASTM Standards*, The American Society for Testing and Materials, Philadelphia, Pp.315-397.
 Baer, E. (1996). *Advanced Polymers*, *Scientific American*, **255(4)**: 178-190.
 Brown, W.H., Foote, C.S. and Iverson, B.L. (2005). *Organic Chemistry*, 4th edn, Thompson Learning, Singapore, Pp.1129-1162.
 Dara, S.S. (2007). *A Textbook of Engineering Chemistry*, 10th Revised edn, S. Chand and Company Ltd, New Delhi, Pp.-360-435.
 Davis, F.J. (2008). *Practical Chemistry: A Practical Approach*, Oxford University Press, Oxford, Pp.319-337.
 McCrum, N.G., Buckley, C.P. and Bucknall, C.B. (1997). *Principles of Polymer Engineering*, Oxford Science Publications, Oxford, Pp.30-37.
 Mihai, M., Huneault, M.A, and Favis, B.D. (2007). Foaming of Polystyrene/Thermoplastic Starch Blends, *Journal of Cellular Plastics* **43**: 215-236.
 Painter, P.C. and Coleman, M.M. (1999). *Fundamentals of Polymer Science: An Introductory Text*, CRC Press, Boca Raton, Pp.183-212.
 Rattan, S. (2007). *Engineering Chemistry (With Experiments)*, 4th edn, S.K. Kataria and Sons, New Delhi, Pp.670-673.
 Rudin, A. (2006). *The Elements of Polymer Science and Engineering*, 2nd edn, Reed Elsevier India Private Limited, New Delhi, Pp.377-444.
 Sperling, L.H. (2006). *Introduction to Physical Polymer Science*, John Wiley and Sons, London, Pp.510-547.
 Varatharajan, B. and Williams, F.A. (2000). Ignition times in the theory of branched-chain Thermal expansion, *Combustion and Flame* **121**: 551-559.