INVESTIGATION OF SYNTHESIS PARAMETERS OF ANTIMONY FLUOROBORATE AND ITS USABILITY AS A FLAME RETARDANT FOR CELLULOSIC FABRICS

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In this study, the synthesis parameters of antimony fluoroborate, one of the metal fluoroborates, from antimony trioxide and fluoroboric acid by the wet method, and its usability as flame retardant for cellulosic fabrics have been investigated. The maximum reaction yield was determined depending on the mole ratio of reactants, temperature and stirring speed. The characterization of the product was performed by XRD and FTIR analyses. Antimony fluoroborate was produced with 94% yield at a mole ratio of reactants ($nHBF_4/nSb_2O_3$) of 6:1, at 70 °C and 300 rpm. The thermal behaviors of untreated fabric and fabric impregnated with antimony fluoroborate solution were analyzed by TGA. The flame retardancy performance of antimony fluoroborate for cellulosic fabrics was determined by the vertical flame test and the limiting oxygen index (LOI) test methods. The results show that impregnating cellulosic fabrics with antimony fluoroborate enhances their thermal stability and flame retardancy.

Keywords: antimony fluoroborate, flame retardant, cellulosic material, LOI

INTRODUCTION

New materials and new methods are constantly investigated to protect humans and their assets from the destructive effects of fire. The development of novel flame retardants is an important research issue. Flame retardants (FRs) are used in large quantities in textile products to increase the safety of people and the environment against a possible fire.[1] With regard to textiles, cotton is among the most frequently used natural cellulosic fibers due to its good biodegradability, softness and permeability. However, cotton is highly flammable. It is the most significant disadvantage of cotton fabric. Therefore, it is of great importance to provide it with flame resistance. Flame retardants amend this deficiency in cotton fabric to ensure the safety of the user.[2,3] For this reason, many researchers have focused on developing new synthetic flame retardants for cotton textile fabrics in recent years.[4]

Flame retardants move in the vapor phase or in the condensed phase via chemical or physical mechanisms, interfering with combustion during heating, pyrolysis, ignition or flame spreading. Each type of fire retardants works in a different way. Flame retardancy of boron compounds is related to the formation of a surface layer of protective char, which acts as a barrier to prevent the oxidation of carbon.[5] Boron compounds, which are active in the condensed phase, represent a significant family of inorganic additives with flame retardant properties and are considered as environmentally friendly when used as flame retardants.[6,7] They are also used in smoke suppression, promoting charring, as multifunctional flame retardants being added as pigment in dyes[8] and in combination with other halogen-free flame retardant systems for their synergistic effect to boost flame retardant properties.[6]

Different types of boron compounds have been reported to be used as flame retardants. Fluoroborates are special boron compounds with flame retardant properties. Various synthesis methods for fluoroborate compounds have been developed. Particularly in industrial production, boric acid and fluoroboric acid are produced with metal halides, oxides, carbonates, bicarbonates and fluorides in different combinations to produce the desired fluoroborates.[9,10] Another method is to react boron fluoride with metal fluorides to form stable fluoroborates.[11] Fluoroborates are also obtained by the mechano-chemical method. Aydın *et al*. produced zinc fluoroborate and copper fluoroborate by high-energy ball milling.[12,13]

Fluoroborates have been widely used in many different applications, as catalysts, flame retardants, optic materials, textiles and plating baths. Fluoroborate baths have a higher limiting current density than other simple salt baths.[14] Moreover, metal fluoroborates are widely used in glasses. Lead fluoroborate increases the electrical conductivity of glass.[15] Lithium, zinc and sodium fluoroborate glasses increase the thermal properties of glasses, such as glass stability factor, with the addition of rare earth elements.[16-19] Metal fluoroborates are very effective when used as catalysts in different reactions. Copper(II) tetrafluoroborate is a highly efficient catalyst for Michael addition.[20] Zinc tetrafluoroborate has high efficiency in the Biginelli reaction.[21] Sodium fluoroborate is used in organic reactions as catalyst.[22] High efficiency has been obtained when sodium tetrafluoroborate was used as catalyst in electrophilic substitution reactions.[23] Pure antimony trisulfide was leached with a ferric fluoborate based electrolyte, which oxidizes sulfide into elemental sulfur and dissolves antimony as antimony fluoborate, in a study to obtain pure sulfur and antimony by the electrolytic process.[24] Hydrometallurgical treatment of metal-containing materials containing more than one metal, such as antimony, lead, copper, zinc, bismuth, tin, cadmium and other metals, can be carried out using a ferric fluoroborate leach solution to separate at least two metals from the metal-containing material. When the fluoborate leach solution contains a significant amount of antimony, other metals are separated from the first raffinate solution. The second raffinate becomes the antimony fluoroborate solution.[25] Fluoroborates perform well when they are utilized as flame retardants. Zinc fluoroborate is used as flame retardant in synthetic fibers, cotton and artificial silk.[26,27]

To clarify the flame retardancy mechanism, many studies have focused on the measurement of thermal decomposition behavior.[28] There are also other test methods, such as LOI, vertical flame test, flame chamber, smoke density *etc*. LOI test can be defined as the amount of oxygen needed to allow the material to continue to burn in the air. The relative flammability of fabric is evaluated under controlled conditions of candle-like flame by the LOI test method.

To the best of the authors' knowledge, there is no study in the literature on the synthesis of antimony fluoroborate and its use as a flame retardant. To fill this knowledge gap in the literature, the aim of the present work has been to investigate the synthesis parameters of antimony fluoroborate and its flame retardancy on cellulosic fabrics assessed by the vertical flame test, LOI test method and thermogravimetric analysis.

EXPERIMENTAL

Antimony fluoroborate was synthesized by the reaction of antimony trioxide (99% pure, Sigma-Aldrich) and fluoroboric acid (50% pure, Acros Organics). The reaction was carried out in Teflon reactors, since fluoroboric acid is corrosive in glass materials. Experiments were conducted at various mole ratios, temperatures and stirring rates.

In order to determine the optimum mole ratio of the reactants (HBF_4/Sb_2O_3), samples were prepared different mole ratios, namely, 6:1, 12:1 and 24:1, at the same temperature. After determining the optimum mole ratio, the effect of temperature (30 °C, 50 °C, 70 °C, 80 °C) on the yield was investigated. Reaction time was fixed as 120 minutes for all experiments. The yield was found according to reaction stoichiometry. The chemical reaction is given as:

$$Sb_2O_3 + 6HBF_4 \rightarrow 2Sb(BF_4)_3 + 3H_2O \quad (1)$$

FTIR (Jasco FTIR-480+) and XRD (Rigaku) were used for characterization of the product. Powder KBr pellets (Merck 104907) were prepared for FTIR and the IR spectra were recorded in the spectral range from 4000 to 650 cm^{-1} at ambient temperature. Antimony fluoroborate solutions were prepared in different percentages (6%, 12%) and used to impregnate cotton fabrics. Fabrics with the same characteristics have been used for the entire study. The characteristics of the fabric samples are given in Table 1.

Table 1
Characteristics of fabrics used in experiments

Material type	100% cotton
Weave type	2x2
Areal density (g/m^2)	437
Weft density (picks/cm)	15
Waft density (ends/cm)	23

The fabrics were left in the solution for a certain time and then dried at 30 °C. Thermogravimetric analysis (TGA) was performed at a heating rate of 10 °C/min within a temperature range from 20 to 800 °C under air atmosphere by using an STA449F3 Jupiter instrument. The flame retardant properties of antimony fluoroborate were investigated by the vertical flame test according to ASTM D6413 and LOI test method according to ASTM D2863 standard. Vertical flame tests were performed on strips of fabric (30 x 7.6 cm). LOI tests were also conducted on strips of fabric (13 x 6 cm). The LOI value of the untreated fabric was determined and compared to that of the fabric impregnated with antimony fluoroborate.

RESULTS AND DISCUSSION

The temperature and stirring speed were kept constant at 50 °C and 300 rpm (revolutions per minute) when determining the optimum mole ratio. The yield was calculated according to the formula given in Equation (2):

$$Yield\ \% = \frac{The\ amount\ of\ produced\ antimony\ fluoroborate,ml}{Theoretical\ amount\ of\ antimony\ fluoroborate,ml} * 100 \qquad (2)$$

The effect of the mole ratio of the reactants on the product yield is depicted in Figure 1. As can be seen, the highest yield was obtained when the reactant mole ratio (n_{HBF4}/n_{Sb2O3}) was 6:1. As the mole ratio increased, a decrease in the yield was observed, because of the dilution effect in the medium. Antimony fluoroborate was produced at the reactant mole ratio of 6:1 and 50 °C with 65% yield.

Antimony fluoroborate was pressed with KBr into pellets for FTIR analysis. The characteristic FTIR absorption band of B-F is in the range of 1000-1100 cm^{-1}.[27] The FTIR technique has been used for both qualitative analysis and quantitative analysis. Figure 2 shows the FTIR spectra of the starting materials. FTIR results were given for different mole ratios in Figure 3a. The strongest peak is noted at the mole ratio of 6:1. These results were obtained when the temperature was fixed at 50 °C. When the molar ratio was increased, it was observed that the peak area of the B-F bond decreased (Fig. 3b). Thus, FTIR results support those obtained experimentally.

The effect of different temperatures (30, 50, 70, 80 °C) on the product yield at the optimum mole ratio was also investigated. Figure 4 illustrates that the product yield enhances with an increasing temperature. This finding has revealed that the reaction is endothermic. The optimum temperature has been determined as 70 °C. However, when the temperature was above 70 °C, the reaction did not occur. The antimony fluoroborate was produced with a 94% yield under the optimum conditions (n_{HBF4}/n_{Sb2O3} = 6:1 and 70 °C).

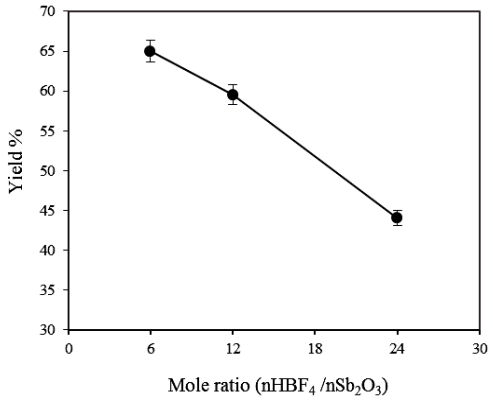

Figure 1: Effect of mole ratio ($nHBF_4/nSb_2O_3$) on product yield

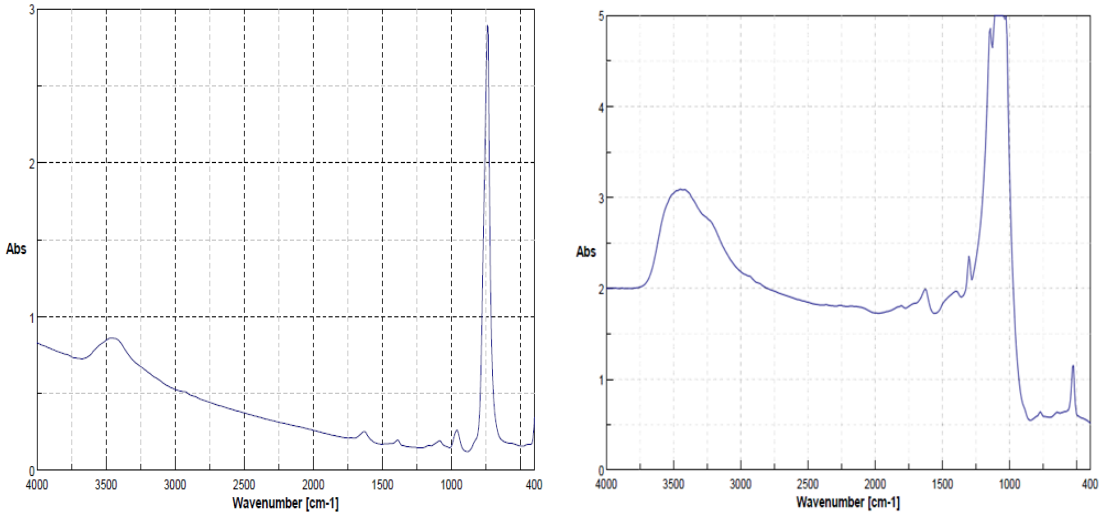

Figure 2: FTIR spectra of (a) antimony trioxide, and (b) fluoroboric acid

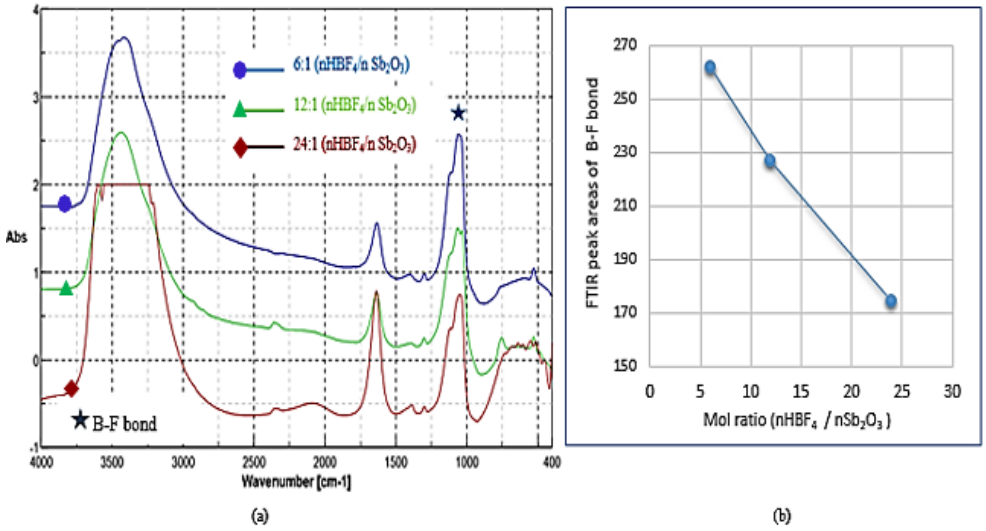

Figure 3: (a) FTIR peaks at different mole ratios, (b) Peak areas of the B-F bond in FTIR spectra at different mole ratios

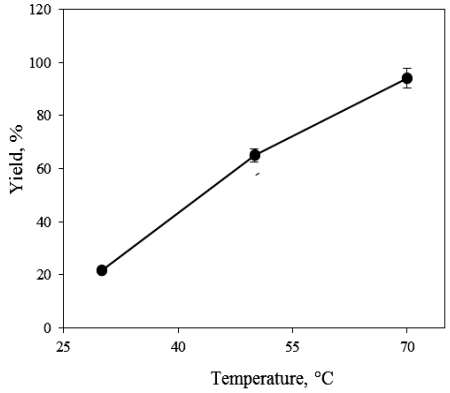

Figure 4: Effect of temperature on the product yield

The FTIR spectra of the samples obtained at different temperatures are given in Figure 5a. The highest peak of the B-F bond was observed at 70 °C and Figure 5b indicates that the highest peak area was found when the temperature was 70 °C. Thus, FTIR results support quantitative experimental results.

After determining the optimum conditions, the reaction was conducted at different stirring rates (300 rpm, 400 rpm and 500 rpm). The same amount of product was obtained at different stirring rates, thus it was concluded that the stirring rate has no effect on the antimony fluoroborate product yield. The XRD analysis graph, showing the crystal structure of the synthesized antimony fluoroborate, is shown in Figure 6.

The thermal stabilities of the untreated fabric and the fabric treated with antimony fluoroborate were determined by TGA analysis. Figure 7 shows the TGA responses in air for both the untreated fabric and the sample impregnated with 12% antimony fluoroborate solution. The TGA curve of the untreated cotton fabric demonstrated a major mass loss of 68% in the range from 310 °C to about 380 °C. Meanwhile, the sample impregnated with antimony fluoroborate lost only about 40% of weight in the same range of temperature. The TGA curves clearly indicate the thermal stability of the treated fabric is higher than that of the untreated original sample. The thermal stability of the materials is related to the initial decomposition behavior and the residual char of the sample in the high temperature range. It has been mentioned that increasing the thermal stability of a working material at high temperature may be associated with improving the flame retardancy.[30]

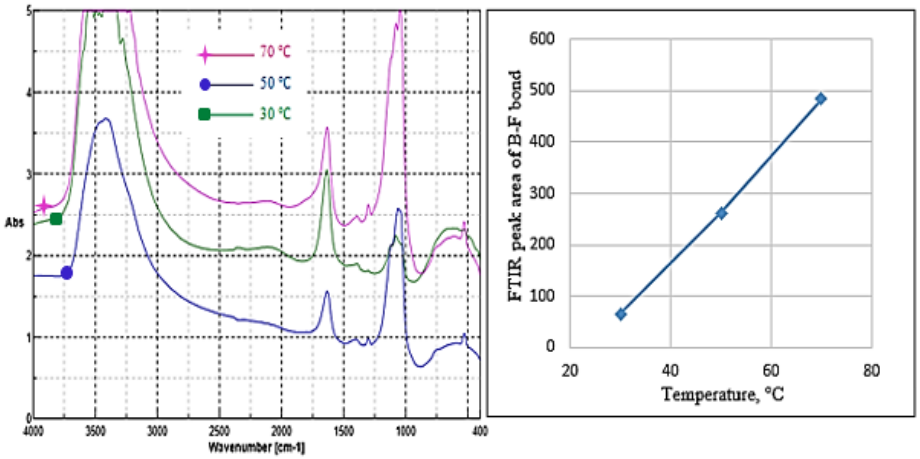

Figure 5: (a) FTIR peaks at different temperatures, (b) Peak areas of B-F bond in FTIR spectra at different temperatures

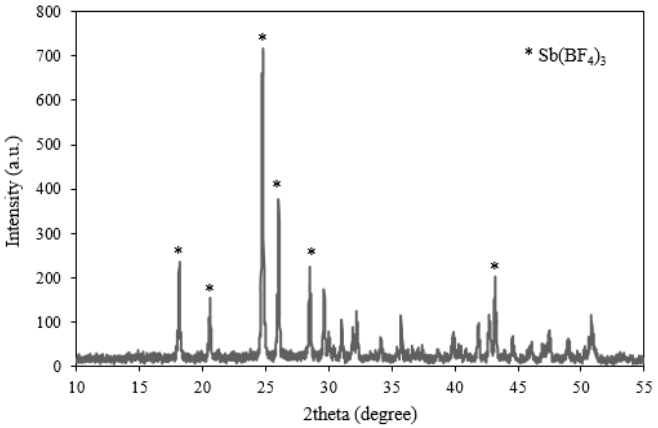

Figure 6: XRD pattern of synthesized antimony fluoroborate

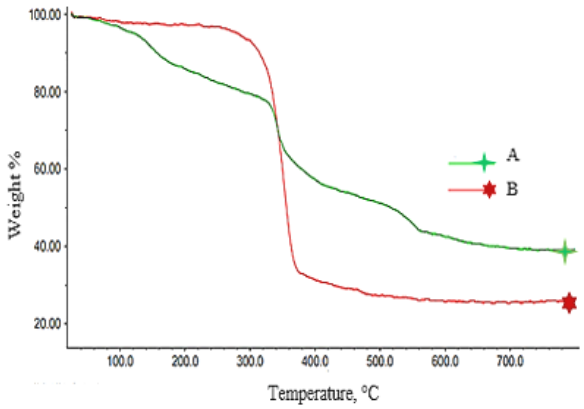

Figure 7: TGA analysis of (A) fabric impregnated with antimony fluoroborate, and (B) untreated fabric

Table 2
Vertical flammability test (ASTM D-6413) of antimony fluoroborate solution impregnated fabrics at different add-on (wt%)

Add-on (wt%)	After-flame time (seconds)	After-glow time (seconds)	Char length (cm)
6%	0	0	5.0-6.0
12%	0	0	3.5-4.0

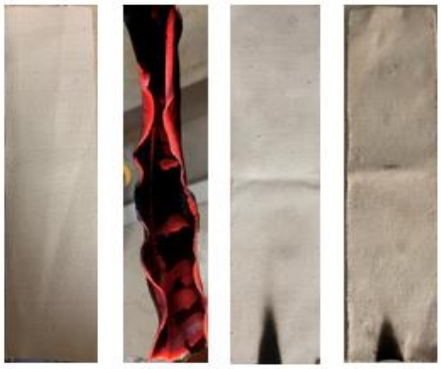

Figure 8: Untreated fabric and vertical flammability test results for (b) untreated, (c) 6% antimony fluoroborate solution impregnated, and (d) 12% antimony fluoroborate solution impregnated fabrics

Vertical flammability test results in Table 2 and Figure 8 demonstrate the effectiveness of antimony fluoroborate as a flame retarder when applied on cellulosic fabrics at add-on levels of 6 and 12 wt%. Antimony fluoroborate impregnated fabrics show flame retardancy even at lower add-on, compared to untreated fabrics. There was no after-flame or after-glow in any of the samples. Char lengths were 5.0-6.0 cm for 6 wt% and 3.5-4.0 cm for 12 wt% add-on.

The flame retardancy effect of the antimony fluoroborate on cellulosic fabric was also determined by the limiting oxygen index test (LOI). The cotton fabrics were impregnated with antimony fluoroborate solutions of 6% and 12% for the LOI test. The impregnation of a flame-retardant solution is usually preferred to surface treatment, because it penetrates below the surface to provide a more effective protection, and its effect lasts longer.[31] The LOI results are tabulated in Table 3.

The LOI test reports the minimum amount of oxygen required to burn a material. A material with a LOI value of more than 21 usually self-extinguishes in the air; a material with a LOI value of less than 21 burns very easily. Therefore, a high LOI value indicates that the material is harder to burn under atmospheric conditions. When antimony fluoroborate was added to the fabric, a significant increase in the LOI results was observed. The results showed that the addition of antimony fluoroborate enhanced the flame retardancy of the fabrics.

Table 3
LOI values of untreated and antimony fluoroborate impregnated fabrics (at different concentrations)

Fluoroborate concentration, %	LOI, O_2 %
Untreated fabric	16
6% Antimony fluoroborate solution impregnated fabric	22
12% Antimony fluoroborate solution impregnated fabric	36

CONCLUSION

Antimony fluoroborate was synthesized by the wet method, which is an economical process, using antimony trioxide and fluoroboric acid. We investigated the effects of reactant mole ratio, temperature and stirring rate as synthesis parameters on the product yield. The maximum yield of 94% was achieved at the reactant mole ratio (n_{HBF4}/n_{Sb2O3}) of 6:1, temperature of 70 °C and stirring rate of 300 rpm. The flame retardancy effect and the thermal behavior of antimony fluoroborate were investigated by the vertical flame and LOI tests, and TGA, respectively. Antimony fluoroborate solutions were prepared at different concentrations and fabrics were impregnated for the tests. TGA results indicate that the treated fabric has higher thermal stability, compared to that of untreated fabric. The fabrics impregnated with antimony fluoroborate solutions passed the vertical flame test when add-on values were 6% and 12%. Their char lengths were less than 50% of the original fabric, with no after-flame and after-glow times. The LOI value of the 12% antimony fluoroborate solution impregnated fabric is more than twice the LOI value of the untreated fabric. The vertical flame test and LOI test results imply that antimony fluoroborate exhibits excellent flame retardancy for cellulosic fabrics.

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