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Original
Degradation of phosphorus based flame retardant by IR radiation / Sohail, Yasin; Giorgio, Rovero; Nemeshwaree, Behary; Anne, Perwuelz; Stéphane, Giraud. - (2015). ((Intervento presentato al convegno AUTEX World Textile Conference 2015.

Availability:
This version is available at: 11583/2670416 since: 2017-05-07T09:16:42Z

Publisher:
AUTEX

Published
DOI:

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DEGRADATION OF PHOSPHORUS
BASED FLAME RETARDANT BY IR
RADIATION

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Biella, Italy.
It is well-known that presence of discarded textile products in municipal landfills pose environmental problems due to leaching of chemical products from the textile to the environment. Incineration of such textiles is considered to be an efficient way to produce energy and reduce environmental impacts of textile materials at their end-of-life stage. However, presence of flame retardant products on textiles would decrease the energy yield and emit toxic gases during the incineration stage. Additionally, some non-durable flame retardants can be removed by wet treatments (e.g., washing), these substances pollute water and pose concerns towards the environmental health. Our study shows that infrared radiation can be used efficiently to degrade flame retardant products on the textiles. This method is finalized to minimize the decrease in energy yield during the incineration or gasification processes of flame retardant cotton fabrics.

The consumption of FRs in Europe in 2006 was 465,000 tons, 10% by weightage of which were brominated FRs [1]. FRs have different chemical composition: they contain halogens (bromine and chlorine), phosphorus, nitrogen, aluminum, magnesium, boron, antimony, molybdenum, or recently developed nano-fillers.

Non-durable flame retardant finishes such as ammonium phosphates are mostly used in disposable medical gowns, curtains and carpets, upholstery, bedding and party costumes [2].

The washed off DAP or APP is a serious threat to the water system and soil. If left on the fabric and discarded for disposal (landfill or incineration) will emanate toxic gases increasing the environmental impact. According to EUROPA & DEFRA [6, 7], a better alternative of disposal is to recycle discarded products rather than producing new ones. When it comes to waste management hierarchy, direct disposals is the least desired option for the wasted and discarded products.

<table>
<thead>
<tr>
<th>Europes FRs consumption in 2006, 465k tons [1]</th>
</tr>
</thead>
<tbody>
<tr>
<td>54% Metal hydroxides</td>
</tr>
<tr>
<td>11% Non-halogen PFRs</td>
</tr>
<tr>
<td>10% Chlorinated PFRs</td>
</tr>
<tr>
<td>9% BFRs</td>
</tr>
<tr>
<td>7% Cholrinate paraffins</td>
</tr>
<tr>
<td>3% Borates and stannate</td>
</tr>
<tr>
<td>3% Antimony trioxide</td>
</tr>
<tr>
<td>3% Melamine based FRs</td>
</tr>
</tbody>
</table>

Waste management hierarchy [6, 7]
Introduction

Sources

In one LCA study, non-durable flame retardants such as ammonium phosphate appeared to have high impact on the environment. The environmental impacts in many categories such as global warming (GWP100), ozone layer depletion (ODP), human toxicity, marine and aquatic ecotoxicity, abiotic depletion and energy use [3, 4]

![Overall impact of ammonium phosphate salt FR from cradle-to-gate life cycle assessment](image)

Objectives

- The aim of this work was to degrade FR from the textile before it goes through incineration process, so it can be used as fuel alternative.
- The proposed pathway of the degradation of FR of the fabric can be a supportive route to decrease environmental impacts as well.
- Incineration of textile products is an efficient way to produce energy using discarded textiles, but incineration of the FR textiles would affect the energy generation and evolves toxic emissions.
- Non-durable FRs can be removed by water treatments, but can pollute the water posing concerns towards environmental sustainability. In addition, the toxicity of FRs is yet to be fully investigated.
Experimental

Materials & Methods

Flame retardant and application
The non-durable FR type, ammonium phosphate dibasic (DAP) with CAS. Number 7783-28-0 was provided by Riedel-de Haën, Germany. The cotton sample used was plain woven dyed 110 g/m² fabric. The FR treated cotton samples were conditioned in dry atmosphere or at 100 % relative humidity (RH).

Infrared emitter
Medium wave (50 Hz) infrared heating element was used, each of them having a maximum heating capacity of maximum 1000 W, 230 V. As the IR heating device has three IR emitters, the total capacity was 3 kW. The rectangular geometric assembly of the IR source used was of 533 mm long (a) and 315 mm wide (b).

View Factor
To evaluate the amount of emitted energy, which reaches the product, a geometric relationship can be used. This expression is called view factor and can be calculated from [8];

\[
F_{1,2} = \frac{2}{\pi XY} \left[ \ln \left( \frac{1 + X^2 + Y^2}{1 + X^2 Y^2} \right) + X \sqrt{1 + Y^2} \tan^{-1} \frac{X}{\sqrt{1 + Y^2}} + Y \sqrt{1 + X^2} \tan^{-1} \frac{Y}{\sqrt{1 + X^2}} - X \tan^{-1} X - Y \tan^{-1} Y \right]
\]

Where, \( X = a/c \) & \( Y = b/c \)

View factors of the IR emitter at different heights

Schematic illustration of FR degradation with IR radiation

Flame test
The flame test results of FR treated cotton dry specimen (1D to 5D samples) and with 100 % RH (1M to 5M samples), shows that samples with 100 % RH subjected to 15-20 minutes IR radiation were completely burnt during the flame test.

Degradation of FR with IR radiation with respect to time

View Factor
The FR treated cotton samples (dry or with 100 % RH) were placed at a distance of 300 mm. At this distance, the cotton sample can intercept 28 % of the radiated energy absorbed from the emitting source.

View Factor
(Fr.1.0)
Discussion & Conclusions

Decomposition of ammonium phosphates has been reported at high temperatures, releasing ammonia or phosphoric acid, depending on environment conditions. It is expected that ammonium phosphate dibasic upon reaching certain temperature on cellulosic materials produces cellulose phosphate by phosphorylation [2]. Ammonium phosphate dibasic as FR needs being saturated by moisture to degrade when subjected to IR radiation.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Weight (g)</th>
<th>Radiation time (min)</th>
<th>Distance burnt (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1D</td>
<td>7.44</td>
<td>0</td>
<td>50</td>
</tr>
<tr>
<td>2D</td>
<td>7.31</td>
<td>5</td>
<td>60</td>
</tr>
<tr>
<td>3D</td>
<td>7.01</td>
<td>10</td>
<td>60</td>
</tr>
<tr>
<td>4D</td>
<td>7.64</td>
<td>15</td>
<td>70</td>
</tr>
<tr>
<td>5D</td>
<td>7.45</td>
<td>20</td>
<td>70</td>
</tr>
<tr>
<td>1M</td>
<td>7.12</td>
<td>0</td>
<td>60</td>
</tr>
<tr>
<td>2M</td>
<td>7.54</td>
<td>5</td>
<td>70</td>
</tr>
<tr>
<td>3M</td>
<td>7.56</td>
<td>10</td>
<td>150</td>
</tr>
<tr>
<td>4M</td>
<td>6.95</td>
<td>15</td>
<td>Complete</td>
</tr>
<tr>
<td>5M</td>
<td>7.42</td>
<td>20</td>
<td>Complete</td>
</tr>
</tbody>
</table>

Flame test of flame retarded samples by IR radiation. Samples in dry conditions (D) and moist conditions (M)

Degradation or removal of the FR finish from textiles can be a suitable route to decrease the environmental impact at their end of life.

IR radiation can be used to degrade FR ammonium phosphate dibasic from the cotton fabrics. Decreasing the distance between the sample and IR emitter enhances the degradation rate.

To maintain the cellulosic nature of cotton unchanged, 15 minute IR radiation time was enough to degrade the FR on the fabric at a certain distance from emitter.

Future perspectives

- Life Cycle Assessment will be conducted hereafter to check the benefits of the method proposed.
- A simple method to improve the energetic yield of a flame retardant textile during incineration, the economical aspect of this step which is preliminary to any thermal treatment has still to be investigated.
- Gasification of discarded textiles is on its way to generate syngas: in this view cotton treated with FR may encounter some difficulty in the process.

Acknowledgments

One of the authors (S.Y) acknowledges with his profound gratitude the European Union's program SMDTex under Erasmus Mundus and technician Mr. Christian Catel, who helped in carrying out some tests presented in this work.

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