Explosibility of Polyamide and Polyester Fibers

ABSTRACT

The current research is aimed at investigating the explosion behaviour of hazardous materials in relation to aspects of particulate size. The materials of study are flocculent (fibrous) polyamide 6.6 (nylon) and polyester (polyethylene terephthalate). These materials may be termed nontraditional dusts due to their cylindrical shape which necessitates consideration of both particle diameter and length.

The experimental work undertaken is divided into two main parts. The first deals with the determination of deflagration parameters for polyamide 6.6 (dtex 3.3) for different lengths: 0.3 mm, 0.5 mm, 0.75 mm, 0.9 mm and 1 mm; the second involves a study of the deflagration behaviour of polyester and polyamide 6.6 samples, each having a length of 0.5 mm and two different values of dtex, namely 1.7 and 3.3. (Dtex or decitex is a unit of measure for the linear density of fibers. It is equivalent to the mass in grams per 10,000 meters of a single filament, and can be converted to a particle diameter.)

The explosibility parameters investigated for both flocculent materials include maximum explosion pressure ($P_{max}$), size-normalized maximum rate of pressure rise ($K_{St}$), minimum explosible concentration (MEC), minimum ignition energy (MIE) and minimum ignition temperature (MIT). ASTM protocols were followed using standard dust explosibility test equipment (Siwek 20-L explosion chamber, MIKE 3 apparatus and BAM oven).

Both qualitative and quantitative analyses were undertaken as indicated by the following examples. Qualitative observation of the post-explosion residue for polyamide 6.6 indicated a complex interwoven structure, whereas the polyester residue showed a shiny, melt-type appearance. Quantitatively, the highest values of $P_{max}$ and $K_{St}$ were obtained at the shortest length and finest dtex for a given material. For a given length, polyester displayed a greater difference in $P_{max}$ and $K_{St}$ at different values of dtex than polyamide 6.6. Long ignition delay times were observed in the BAM oven (MIT measurements) for polyester, and video framing of explosions in the MIKE 3 apparatus (MIE measurements) enabled observation of secondary ignitions caused by flame propagation after the initial ignition occurring at the spark electrodes.

1. INTRODUCTION

The purpose of the current research is the prevention and mitigation of dust explosions based on the strategic area of safety and security, with a focus on assessing risk and vulnerability. The main motivation for developing this research topic is the protection of personnel, assets, production (business operation) and the environment. By adopting the recommendations arising in this study, industries could reduce and
minimize their current dust explosion risk as well as the probability of future occurrences of explosions.

There have been numerous cases of dust explosions over the years, with reported incident data illustrating that dust explosions can occur with a variety of commodities. These include: wood and paper products (dust from sawing, cutting and grinding), grain and foodstuffs (grain dust and flour), metal and metal products (metal powders and dusts), power generation products (pulverized coal, peat and wood), rubber, chemical process industry products (acetate flake, pharmaceuticals, dyes and pesticides), plastic/polymer production and processing products, mining products (coal sulphide ores and sulphur), and textile manufacturing products (linen flax, cotton and wood) (Amyotte and Eckhoff, 2010; Frank, 2004). The first case of a recorded dust explosion was in a wheat flour warehouse in Turin, Italy, as recounted by Count Morozzo in 1785 (Eckhoff, 2003). The report mentioned the destruction of the warehouse due to a primary explosion and successively a secondary explosion.

Dust explosions are a serious hazard in any industry. In the United States alone, the U.S. Chemical Safety and Hazard Investigation Board (CSB) has identified 281 combustible dust incidents between 1980 and 2005 that killed 119 workers and injured 718 more (CSB, 2006). In addition to worker fatalities and injuries, there is also a significant economic impact due to these industrial incidents. The CSB reports damages costing hundreds of millions of dollars for explosions, for instance, at Malden Mills, CTA Acoustics, West Pharmaceutical and Rouse Polymeries (CSB, 2006). One of the key factors for significantly reducing dust explosion hazards is prevention. To accomplish this, it is important to perform adequate housekeeping, as excessive dust accumulation can cause secondary dust explosions (CSB, 2006; Frank, 2004), which can in turn cause significant damage.

Recent incidents have demonstrated the hazards of flocculent (fibrous) materials, which have a cylindrical shape necessitating consideration of both particle diameter and length. The aim of this paper is to provide additional data and knowledge on this nontraditional category of dust. Flocculent materials are not always considered as potential dust explosion hazards; the above-mentioned dust explosion involving nylon flock fibers at the Malden Mills facility in Massachusetts in 1995 (CSB, 2006) demonstrates that they should be viewed in the same light as more traditional dusts composed of spherical or near-spherical particles.

The overall scope of this experimental work includes:

- Studying explosibility characteristics of flocculent materials for different shapes of fibers and types of material.
- Generating experimental data for different sizes of flocculent dusts.
- Exploring empirical relationships between the explosibility data and aspect ratio features of length and diameter.
- Carrying out phenomenological analysis.
2. SAMPLES
The samples investigated were flocculent (fibrous) polyamide 6.6 (polyhexamethylene adipinamide, CAS Nr. 32131-17-2) and polyester (polyethylene terephthalate, CAS Nr. 25038-59-9). Experiments were conducted using the most common dtex (3.3) of polyamide 6.6 with changing length, and successively experiments with changing dtex. (Dtex or decitex is a unit of measure for the linear density of fibers. It is equivalent to the mass in grams per 10,000 meters of a single filament, and can be converted to a particle diameter.) Further experiments were conducted on polyester fibers – the most commonly used material in the textile industry due to its unique properties and low material cost. The decision to analyze these fibers with changing length or diameter (keeping the other parameter constant) was made to better understand the role of specific surface area with respect to deflagration parameters and explosibility characterization of the materials.

The experimental work undertaken can be divided into two main parts. The first deals with the determination of deflagration parameters for polyamide 6.6 (dtex 3.3) for different lengths: 0.3 mm, 0.5 mm, 0.75 mm, 0.9 mm and 1 mm; the second involves a study of the deflagration behavior of polyester and polyamide 6.6 samples, each having a length of 0.5 mm and two different values of dtex, namely 1.7 and 3.3.

3. DETERMINATION OF EXPLOSION PARAMETERS
Explosibility parameters investigated were the maximum explosion pressure ($P_{\text{max}}$), maximum rate of pressure rise (($dP/dt)_{\text{max}}$), size-normalized maximum rate of pressure rise ($K_{St}$), minimum exploisible concentration (MEC), minimum ignition energy (MIE) and minimum ignition temperature (MIT). ASTM (American Society for Testing and Materials) protocols were followed using standard dust explosibility test equipment (Siwek 20-L explosion chamber, MIKE 3 apparatus and BAM oven). Apparatus and procedural descriptions can be found on the equipment manufacturer’s (Kuhner’s) web site (http://www.kuhner.com/).

3.1 Siwek 20-L chamber
A Siwek 20-L explosion chamber was used to determine $P_{\text{max}}$, $(dP/dt)_{\text{max}}$, $K_{St}$ and MEC for the various polyamide 6.6 and polyester samples. Testing protocols followed were according to ASTM E1226-10 (ASTM, 2010) for the first three parameters, and ASTM E1515-07 (ASTM, 2007) for MEC. Because of the low bulk density of the flocculent samples, a test procedure was developed for the 20-L chamber in which a maximum of 15 g of dust were placed in the external dust storage container. This corresponds to a dust concentration of 750 g/m$^3$; for higher concentrations, the remainder of the sample amount was placed directly in the 20-L chamber around the rebound nozzle used for dust dispersion.

Most of the tests carried out here resulted in weak explosions in terms of the rate of pressure rise. If $(dP/dt)_m$ (maximum rate of pressure rise for a given test) is less than 150 bar/s, it is possible that the rate of pressure rise of the chemical igniters used as
the ignition source will be higher than that of the actual dust explosion. Figure 1 shows two inflection points where the first is caused by the pressure rise of the igniters and the second by the flock explosion. In cases such as this, it is necessary to perform a manual evaluation to identify the rate of pressure rise due to the flock explosion rather than relying on the Kuhner-provided software.

![Example pressure/time trace for flock explosion.](image)

### 3.2 Modified Hartmann tube (MIKE 3)
A modified Hartmann tube (MIKE 3 apparatus) was used to determine the minimum ignition energy (MIE) of the samples. Procedures according to ASTM E2019-03 (ASTM, 2003) were followed. MIE values measured with the MIKE 3 apparatus can be reported as either falling within a specified range, or with sufficient tests at ignition and non-ignition boundaries, as a single value (termed the statistic energy and determined by the Kuhner-provided software).

### 3.3 BAM oven
A BAM oven was used to determine the minimum ignition temperature (MIT) of the samples. Procedures according to ASTM E1491-06 (ASTM, 2006) were followed.

### 4. RESULTS AND DISCUSSION
Explosibility data for the polyamide 6.6 and polyester samples are given in Tables 1 and 2. Values of MIE shown in Tables 1 and 2 were determined with inductance.

<table>
<thead>
<tr>
<th>d tex</th>
<th>Length [mm]</th>
<th>( P_{\text{max}} ) [bar(g)]</th>
<th>( (dP/dt)_{\text{max}} ) [bar/s]</th>
<th>( K_{\text{St}} ) [bar·m/s]</th>
<th>MEC [g/m³]</th>
<th>MIE [mJ]</th>
<th>MIT [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.3</td>
<td>0.3</td>
<td>7.1</td>
<td>178</td>
<td>48</td>
<td>75</td>
<td>580</td>
<td>475</td>
</tr>
<tr>
<td>3.3</td>
<td>0.5</td>
<td>6.6</td>
<td>135</td>
<td>37</td>
<td>125</td>
<td>&gt;1000</td>
<td>485</td>
</tr>
<tr>
<td>3.3</td>
<td>0.75</td>
<td>6.4</td>
<td>102</td>
<td>28</td>
<td>155</td>
<td>&gt;1000</td>
<td>485</td>
</tr>
<tr>
<td>3.3</td>
<td>0.9</td>
<td>6.3</td>
<td>102</td>
<td>28</td>
<td>160</td>
<td>&gt;1000</td>
<td>485</td>
</tr>
<tr>
<td>3.3</td>
<td>1.0</td>
<td>6.4</td>
<td>94</td>
<td>26</td>
<td>165</td>
<td>&gt;1000</td>
<td>490</td>
</tr>
</tbody>
</table>
Table 2 Deflagration parameters with changing diameter.

<table>
<thead>
<tr>
<th>Material</th>
<th>dtex</th>
<th>Length [mm]</th>
<th>$P_{\text{max}}$ [bar(g)]</th>
<th>$(dP/dt)_{\text{max}}$ [bar/s]</th>
<th>$K_{\text{St}}$ [bar·m/s]</th>
<th>MEC [g/m$^3$]</th>
<th>MIE [mJ]</th>
<th>MIT [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyamide 6.6</td>
<td>1.7</td>
<td>0.5</td>
<td>6.6</td>
<td>183</td>
<td>50</td>
<td>50</td>
<td>540</td>
<td>485</td>
</tr>
<tr>
<td>Polyamide 6.6</td>
<td>3.3</td>
<td>0.5</td>
<td>6.6</td>
<td>135</td>
<td>37</td>
<td>125</td>
<td>&gt;1000</td>
<td>485</td>
</tr>
<tr>
<td>Polyester</td>
<td>1.7</td>
<td>0.5</td>
<td>6.9</td>
<td>247</td>
<td>67</td>
<td>70</td>
<td>330</td>
<td>495</td>
</tr>
<tr>
<td>Polyester</td>
<td>3.3</td>
<td>0.5</td>
<td>5.5</td>
<td>104</td>
<td>28</td>
<td>70</td>
<td>390</td>
<td>495</td>
</tr>
</tbody>
</table>

4.1 Analysis of explosion data and consideration of specific surface area
The specific surface area (surface area per unit volume) for a cylinder is calculated as follows:

\[
S = \frac{2\pi D^2}{4} + \frac{\pi D L}{\pi D^2 L} = \frac{2}{L} + \frac{D}{D}
\]

Simplifying:

\[
S = \frac{2}{L} + \frac{4}{D}
\]

(for large length-to-diameter ratios: $S \sim \frac{4}{D}$ (Eckhoff, 2003))

If $D$ is constant:

\[
S = \left(\frac{2}{L} + \frac{B}{D}\right)
\]

where $B$ is a constant.

Increasing the length in this case results in a decrease in specific surface area. For this scenario, lower values of $P_{\text{max}}$ and $K_{\text{St}}$ were determined for polyamide 6.6 (Table 1); tests on different lengths of polyester were not conducted. Also with this scenario (increasing length at constant diameter), other parameters such as thermal conductivity may be lower – in which case more time would be required for heat to propagate along the longer covalent fiber bonds. This would result in lower rates of conductive and convective/radiant heat transfer inside and outside the fibers, respectively, ultimately leading to lower energy release rates through fiber combustion.

If $L$ is constant:
Increasing the diameter (dtex) in this case results in a decrease in specific surface area. For this scenario, lower values of $P_{\text{max}}$ and $K_{St}$ were determined for polyester, while polyamide 6.6 showed the same value of $P_{\text{max}}$ and a lower $K_{St}$ value (Table 2).

It is also important to consider the bulk density ($\rho_b$) when attempting to understand the results; bulk density decreases as $L/D$ increases. This non-constant feature of bulk density must influence the explosion results because it has a definite impact on the experimental procedure in terms of material volume to be dispersed for a given mass of dust. Although this influence is difficult to quantify, it can be said that the total specific surface area should include the bulk density as follows:

$$S_{\text{tot}} = \frac{\sum S_i \cdot n_i}{\rho_b \sum V_i \cdot n_i}$$

where $S_i$ and $V_i$ are respectively the surface area and volume of each flock (fiber) and $n_i$ is the number of flocks (fibers) in the total volume considered.

The difference between the behaviour of the two polymers likely results from their different chemical structures. The presence of phenyl groups in the polyester structure may be key to understanding the greater influence of dtex on $P_{\text{max}}$ and $K_{St}$ for this material than for the polyamide 6.6. Moreover, the structure of polyester could lead to a reduced tendency to coagulate and produce a sort of polymeric network – the formation of which would be expected to affect dispersion and increase the MIE. The data in Table 2 support this concept; the MIE for polyester is seen to undergo a far less significant change than for polyamide 6.6 with an increase in dtex. Further support for the argument advanced here is given by the scanning electron micrographs (SEMs) discussed in a subsequent section of the paper. These images (post-explosion) clearly show the tendency of polyamide 6.6 to form a polymeric network, whereas polyester does not display similar behaviour. As illustrated in Table 2, the two materials tested have different hazard profiles when the data are considered in terms of likelihood of explosion occurrence (MEC, MIE and MIT) and severity of explosion consequences ($P_{\text{max}}$ and $K_{St}$).

The data in Table 1 also suggest a characteristic length for polyamide 6.6 beyond which the explosibility parameters do not change significantly. As noted previously, conductive heat transfer within the fibers is a function of the material’s thermal conductivity. Higher values of thermal conductivity are found in metal particles due to delocalization of the electrons on the surface. Although the thermal conductivity for polymers has lower values due to their covalent structure, studies have shown that the
degree of thermal conductivity is connected to elongation (Novichenok and Ovchinnikiva, 1982). During the elongation process in producing the fiber, an orientation of covalent bonds occurs due to anisotropic properties; thermal conductivity reaches higher values in the direction of the orientation. Understanding this phenomenon therefore helps in understanding the potential hazards of fiber explosions; the value of fiber L/D can strongly influence the rate of heat transfer. Lower values of thermal conductivity require a longer time for propagation of heat along covalent fiber bonds. This results in lower rates of conductive heat transfer inside the fibers and hence a lower energy release rate through fiber combustion. This is reflected in the weaker explosions brought about by an increase in fiber length (to a limiting value).

4.2 First session experiments – data trends and explanation
In this section we present graphically some of the polyamide 6.6 (dtex 3.3) explosibility data given in Table 1, and provide further commentary on the experimental results. Figures 2 – 4 illustrate the trends in \( P_{\text{max}} \), \( K_{\text{St}} \) and MEC, respectively. (The data trend for \((dP/dt)_{\text{max}}\) is of course the same as that shown in Figure 3 for \( K_{\text{St}} \).) The aforementioned concept of a characteristic length for these samples is evident in Figures 2 – 4 at \( L = 0.75 \) mm.

**Figure 2** \( P_{\text{max}} \) as a function of length for polyamide 6.6.

**Figure 3** \( K_{\text{St}} \) as a function of length for polyamide 6.6.
The MIE results in Table 1 indicate that only the finest fibers of polyamide 6.6 (dtex 3.3) could be ignited in the MIKE 3 apparatus (with a spark energy of 1 J being the maximum attainable with this equipment). The 0.3-mm long polyamide 6.6 ignited at 1000 mJ but not at 300 mJ (yielding a statistic energy of 580 mJ) with an ignition delay time of 180 ms (low turbulence). As previously mentioned, a possible reason for the increase in MIE with increasing fiber length is an enhanced tendency for the flock to coagulate and form aggregates – thereby reducing dust dispersion and affecting ignition energy requirements (Marmo and Cavallero, 2008; Worsfold et al., 2012).

An additional reason for increased MIE values with longer fibers is the melting process, which causes softening and deformation of the flock prior to ignition. Polyamide 6.6 fibers typically have a low melting temperature (260 °C). This value is significantly lower than the MIT values shown in Table 1, which display a narrow range for the lengths investigated.

### 4.3 Second session experiments – data trends and explanation

In a similar manner, here we present graphically some of the polyamide 6.6 (L = 0.5 mm) and polyester (L = 0.5 mm) explosibility data given in Table 2, and provide further commentary on the experimental results. Figures 5 – 7 illustrate the trends in $P_{\text{max}}$, $K_{\text{St}}$ and MEC, respectively.

**Figure 4** MEC as a function of length for polyamide 6.6.

**Figure 5** $P_{\text{max}}$ as a function of dtex for polyamide 6.6 (diamond) and polyester (square).
Polyester (dtex 3.3) displays the lowest values of $P_{\text{max}}$ and $K_{\text{St}}$ among all the 0.5-mm long samples investigated. Alternatively, the other polyester sample (dtex 1.7) has the highest values of these parameters. Figures 5 and 6 suggest that overall, fiber diameter has a more significant effect on $K_{\text{St}}$ than on $P_{\text{max}}$ for both materials studied.

With respect to minimum explosible concentration (Figure 7), fiber diameter (dtex) has no effect on the polyester samples; the polyamide 6.6 MEC is seen to undergo a pronounced increase with an increase in dtex from 1.7 to 3.3.

While the minimum ignition temperatures shown in Table 2 are similar for all four samples, a different pattern is evident with respect to minimum ignition energy. Fiber diameter plays a major role in determining the spark energy required for ignition of polyamide 6.6, and much less so for polyester, for the reasons discussed previously. Similar results were obtained for these same materials by von Pidoll (2002).

4.4 Scanning electron microscopy (SEM)
A scanning electron microscope (SEM) was used to provide images of the tested samples both pre- and post-explosion. With this technique, the area to be examined is irradiated with a focused electron beam and signals are produced by interaction of the electron beam and the sample. These signals include secondary electrons,
backscattered electrons and other photons. In particular, secondary and backscattered electron contrast permits examination of sample characteristics such as surface topography, crystallography and composition (Goldstein et al., 2003).

Polyamide 6.6 and polyester are organic polymers that become charged during scanning electron microscopy. At high magnification (>1000x), it is therefore necessary to employ a gold coating process to avoid the formation of electrical charging (Goldstein et al., 2003). The SEM analyses in the current work were conducted without a coating process because it was not important to study the sample at highest magnification; in this way damage of the samples by metal coating was avoided. Low magnification was sufficient to assess the surface characteristics before and after the explosion of the materials.

Scanning of the fibers before explosion was helpful in understanding the particle size distribution and the shape of flocculent material. Figure 8 shows polyamide 6.6 (dtex 3.3 and L = 0.5 mm) under low magnification. The fibers display a cylindrical shape due to the flock cutting process; this is in agreement with the notion of using a cylinder to determine specific surface area.

![Micrograph of polyamide 6.6 (dtex 3.3 and L = 0.5 mm) before explosion.](image)

**Figure 8**  Micrograph of polyamide 6.6 (dtex 3.3 and L = 0.5 mm) before explosion.

Post-explosion micrographs help to explain the difference in deflagration behaviour of polyamide 6.6 and polyester. Polyamide 6.6 shows an expansive network due to melting fibers. The cylindrical fibers change their shape, becoming shorter and thicker. (See Figure 9.) Moreover, they also have a greater tendency to coagulate and form spherical or near-spherical aggregates. (See Figure 10.) This demonstrates the ability of polyamide 6.6 to form structures of spherical morphology due to its chemical nature.
SEM analysis of polyester post-explosion shows the appearance of different kinds of surfaces. Here, the high temperatures cause melting in some areas, whereas the remaining areas appear to have fewer interactions and network formation. (See Figures 11 and 12 for representative polyester post-explosion micrographs).
Wider zones show that a large quantity of polyester fibers did not melt even though their structure changed. In fact, it is possible to observe some fibers longer than in the raw flock. (See Figure 13.) This again indicates the reduced tendency of polyester to coagulate and also illustrates the role that material composition plays in determining the minimum ignition energy. A
milder melting network results in a less significant effect on MIE when the diameter of the flock is increased.

**Figure 13** Micrograph of polyester after explosion.

### 4.5 Phenomenological analysis

Long ignition delay times for polyester were observed in the BAM oven during the MIT experiments. Because the ignition criterion with this device is flame propagation out of the oven within 5 s of dust dispersal, this means that smoldering combustion can be an important consideration with flocculent materials.

Video framing of explosions in the MIKE 3 apparatus (MIE measurements) enabled observation of secondary ignitions caused by flame propagation after the initial ignition occurring at the spark electrodes. Figures 14 – 17 show four frame sequences for polyamide 6.6 (dtex 1.7 and L = 0.5 mm). The particular test was conducted with a dust amount of 1200 mg and an ignition delay time of 120 ms.

Ignition of the flock first occurs (Figure 14), followed by flame propagation vertically in the glass tube (Figure 15). During these two steps, there are no flames at the bottom of the apparatus. Some of the dust lies at the bottom of the tube, however, and is ignited by backfire (Figure 16). Hence, there is a secondary ignition and further propagation of flames (Figure 17). Afterward, a sticky, interwoven residue structure was found coating the interior of the glass tube.

The delay time required to ignite the fibers, as well as their flame propagation pattern, are both important elements in understanding the hazardous nature of flocculent materials. The persistent flame that can result represents a possible source of ignition
to other flock present in an industrial process. Some flocculent material may take part in the initiating event, while other flock may participate in successive stages. Consideration of both explosion and fire risks are essential for this class of nontraditional dusts.

Figure 14  Primary ignition of polyamide 6.6 (dtex 1.7 and L = 0.5 mm).

Figure 15  Primary flame propagation of polyamide 6.6 (dtex 1.7 and L = 0.5 mm).
5. CONCLUSION
The values of the explosibility parameters ($P_{\text{max}}$, $K_{\text{Sr}}$, MEC, MIE and MIT) investigated for both flocculent materials are indicative of the dust explosion hazards associated with each. Consideration of the effect of fiber diameter (dtex) and length on specific surface area is key to understanding the magnitude of these parameters, as is the actual chemical composition of the material.
Scanning electron microscopy has been shown to be useful in further interpretation of the quantitative results obtained experimentally. Phenomenological analysis of the actual experimentation is also helpful in better understanding the nature of the fire and explosion hazards posed by flocculent materials.

The challenge now is to assist the flock handling and processing industry in minimizing both the likelihood and severity of dust explosions. By investigating the explosion behavior of hazardous materials in relation to aspects of particulate size, it is possible to recommend that good housekeeping and cleanup of flocculent materials in facilities that produce them (either as a principal product or as a byproduct) are fundamental to avoid dust fires and explosions. Moreover, fine flock (smaller dtex and shorter length) are more hazardous and easily ignitable than larger flock sizes.

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REFERENCES