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Effect of Silicone Finishes on the Burning Behavior of Polyester

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ABSTRACT

Polyester fibers are widely used as filling in home applications such as pillows or comforters. Silicone finishes can be used to reduce friction between fibers during processing or as softeners to impart a pleasant down like hand on the fibers. However, it has been reported that these added silicone-based finishes may have a negative effect on the burning behavior of polyester. This research examined the possible mechanisms that can modify the response of polyester fibers when subjected to a flame source. In this study, a spunbond needled polyester nonwoven substrate was treated with different commercial silicone-based finishes. A vertical flame test was used to compare the effect of silicone finishes on the burning behavior of polyester to the inherent burning behavior of untreated polyester. Thermogravimetric analyses (TGA) were performed on spunbond polyester fabric samples to investigate the influence of silicone finishes on the thermal degradation of polyester in air. Residues from TGA were examined using Scanning Electron Microscopy coupled with elemental analysis. Vertical flammability testing showed that even at a low level, the application of silicone-based finishes on a polyester substrate resulted in a dramatic increase of the flame propagation by preventing its inherent response to heat. Thermograms suggested that the silicone finishes had little or no effect on the thermal degradation of polyester substrates.
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CHAPTER 1

INTRODUCTION

1.1 Polyester

1.1.1 Generalities

In rule 16 of the Code of Federal Regulations (CFR) part 303.7 (c), the Federal Trade Commission (FTC) defines a polyester fiber as a “manufactured fiber in which the fiber forming substance is any long-chain synthetic polymer composed of at least 85% by weight of an ester of a substituted aromatic carboxylic acid, including but not restricted to

\[
\begin{align*}
\text{Figure 1.1: Reproduction of substituted terephthalic unit} \\
\text{defined by FTC (adapted from FTC [1])}
\end{align*}
\]

substituted terephthalic units, and parasubstituted hydroxy-benzoate units” [1].

\[
\begin{align*}
\text{Figure 1.2: Reproduction of parasubstituted} \\
\text{hydroxy-benzoate unit defined by FTC} \\
\text{(adapted from FTC [1])}
\end{align*}
\]

In this discussion, unless otherwise specified, the term polyester will refer to poly(ethylene terephthalate) commonly known as PET. Figure 1.3 shows a more standard representation of the PET repeat unit as encountered in academia. In 2012 the worldwide production of polyester fibers reached 41,440,000 tons which represents 49.9% of the total worldwide production of all fibers [2].
Polyester fibers tend to accumulate static charges because their moisture regain is relatively low (0.4%) [3]. Moisture regain is the mass of water in a material expressed as a percentage of the oven dry mass of that material [4].

\[
\text{Regain} = \frac{100 \times W}{D} \%
\]  

(1)

Where

D = dry sample mass
W = mass of absorbed water at 20°C and 65% Relative Humidity (RH).

Polyester fibers used in staple form have a specific gravity of 1.38 [5]. Typical fiber sizes used in fiberfill range from 4 to 6 denier [6]. Denier is a unit of linear density commonly used in the American textile industry whereas Europe uses mostly the tex system. Denier describes the fineness of fibers, filaments and yarn and in grams is equal to the weight of 9,000 meters of material [7].

\[
\text{Denier} = \frac{m}{9000 \times l}
\]  

(2)

Where

l = length in meter of a material of mass m in grams.

Since Tex is equal to the weight in grams of 1,000 meters of material, the conversion is shown in equation (3).
Polyester molecular weights normally used for fiber production range from about 15,000 to 25,000 g.mol\(^{-1}\) [8].

1.1.2 Fiberfill

Fiberfill refers to manufactured fibers made specifically for use as filling material in household textiles such as pillows, comforters, mattresses, sleeping bags, seat cushions and outdoor furniture [7]. Polyester fibers are widely employed in this type of application. A few examples of fibers made by Invista for bedding:

- COMFOREL® fiberfill, “that provides luxurious softness and support” [9];

- Performa® fiberfill, “providing added firmness and freshness” [10];

- Duralife™ fiberfill, ”an excellent bulk and high-fill power fiber” [11].

These fibers are advertised as having great loft, resiliency, soft feel, and luxurious hand. Manufacturers emphasize the softness argument to promote similarities to down. Down is “the fine soft covering of fowls, forming the under plumage, used for stuffing beds, pillows, etc” [12]. One way to achieve these properties is through the use of silicone-based finishes.

1.2 Silicones

1.2.1 Definition

According to the International Union of Pure and Applied Chemistry (IUPAC),
the term silicones refers to “polymeric or oligomeric siloxanes, usually considered unbranched, of general formula \([-\text{OSiR}_2-]_n\) (R\(\neq\)H)” [13], with siloxanes defined as “saturated silicone-oxygen hydrides with unbranched or branched chains of alternating silicone and oxygen atoms (each silicon atom is separated from its nearest silicon neighbors by single oxygen atoms). The general structure of unbranched siloxanes is \(\text{H}_3\text{Si}[\text{OSiH}_2]_n\text{OSiH}_3\) [14]. From the industry standpoint, the word silicone is also sometimes more loosely used for a polymer having the general formula \((\text{R}_n\text{SiO}_{4-n/2})_m\) with \(0\leq n\leq 3\) and \(m\geq 2\). The term originated in 1901 from the initial assumption that the compound had a structure \(\text{R}_2\text{Si}==\text{O}\) similar to ketones in carbon chemistry [15,16].

![Figure 1.4: Structure of conventional polydimethylsiloxanes](image)

In the large family of polysiloxanes, linear polydimethylsiloxanes (PDMS) are the most important and the most conventional ones in the industry. In fact, it is often assumed that PDMS is the one referred to when the general “silicone” term is employed. However, one needs to be more specific when describing a component since their usage will differ depending upon their end groups. Typical silicone fluids are trimethylsilyl-terminated PDMS such as methylsilicone fluids having the structural formula displayed in Figure 1.4 \((n=2-4000)\). Other types of PDMS can have end groups such as –OH, –H or –CH==CH\(_2\).
1.2.2 Properties

Silicone fluids exhibit good thermal stability in air with little change seen in the physical properties up to 200°C as well as a high solubility to gases and a strong hydrophobicity [17]. Their thermal stability stems from the high Si–O bond strength, 475 kJ.mol⁻¹, compared to carbon-carbon bonds (346 kJ.mol⁻¹). Commercially, they are usually classified based upon their viscosity determined by the average chain-length. In one example, the available viscosities range from 0.65 centiStokes (cSt) to 20,000,000 cSt. It should be noted that above a molecular weight of 30,000 g.mol⁻¹ (or a viscosity of 1000cSt), the physical properties dependent upon the change in viscosities such as refractive index, surface tension, density and viscosity-temperature coefficients reach a plateau [18]. Stokes is the unit of kinematic viscosity, corresponding to cm².sec⁻¹ in SI units. Values can also be found expressed as dynamic viscosity, Pa.s in SI units, depending upon the manufacturer location. The Poise (P) unit is sometimes used for dynamic viscosity as well, with 1 P = 0.1 Pa.s. For instance, the viscosity of water at 20°C is 10⁻³ Pa.s or 1 cP (centiPoise) or 1cSt. Equation (4) shows the conversion between kinematic and dynamic viscosity.

\[ \nu = \frac{\eta}{\rho} \]  

(4)

Where

\( \nu \) = kinematic viscosity
\( \eta \) = dynamic viscosity
\( \rho \) = fluid density

(The letter \( \mu \) is also used to expressed viscosity)

For molecular weight greater than 2,500 g.mol⁻¹, a linear relationship has been
established through the Barry equation between the fluid viscosity and its molecular weights, as shown in Figure 1.5.

Silicones properties can be tailored to specific needs by modifying the organic side groups, such as \((\text{CH}_3)_3\text{Si-O-[Si(\text{CH}_3)_2-O]}_n-[\text{RSiCH}_3-O]_m-\text{Si(\text{CH}_3)}_3\). When R is an amino functional group (-R₁-NH-R₂-NH₂), silicones are used as fabric softeners. Amino-functional silicones are usually found in emulsion formulations, microemulsions being the most appropriate in the case of microfibers. Table 1.1 shows the different markets where these finishes are used. Typical application levels of aminofunctional silicones range from 0.25% to 1% based on the weight of fabric [19]. In polysiloxane
water-repellent applications, treatments aim at leaving between 1% to 2% of silicone finish on the fibers [20].

Table 1.1: Finishing demands on microfiber fabrics (adapted from Mooney [19] table 7.12)

<table>
<thead>
<tr>
<th>End-use</th>
<th>Garment types</th>
<th>Finish requirements</th>
</tr>
</thead>
<tbody>
<tr>
<td>Outerwear</td>
<td>Slacks, dresses, shirts, blouses, skirts, jackets</td>
<td>Supersoft, excellent drape, easy care, light-weight, dimensional stability, comfort</td>
</tr>
<tr>
<td>Sportswear</td>
<td>Raincoats, anoraks, ski jackets, sailing wear, track suits, sweat suits</td>
<td>Water-repellent, air permeable, wind-tight, light-weight, soft, easy-care, dimensional stability</td>
</tr>
<tr>
<td>Technical</td>
<td>Sleeping bags, tents, shades, workwear, filters, car upholstery</td>
<td>Softness, dye fastness, light fastness, drape, easy-care, low soil, low fogging</td>
</tr>
</tbody>
</table>

In the case of polyester, the hydrophobic segments of the silicone chains interact with the hydrophobic fiber surface, these interactions resulting in an evenly distributed silicone film on the fiber surface as shown in Figure 1.6. Desirable properties such as a good hand, water repellency and high softness can thus be achieved. The hand of a fabric is a rather subjective assessment of its tactile quality, the way it feels, how we react to the touch [21].
Silicones can be used at several steps in the textile industry, such as fiber production, fabric softeners or process aids, depending upon the material properties and the substrate. During fiber production, silicone lubricants serve as process aids for man made fibers to reduce friction since they not have any natural lubricants. These lubricants can either be used to reduce friction between fibers and pieces of machinery or between the fibers themselves. The later case is usually seen for fiberfill production when fibers are encapsulated by a three-dimensional crosslinked silicone based network [22]. Fabrics can also be treated directly with silicone softeners such as aminofunctional silicone fluids [23]. When used as process aids, silicones can be employed as antifoaming agents.

In order to wet a solid surface, the surface tension of the liquid must be lower than the critical surface tension of the substrate. For instance, water has a surface tension of 72 mN.m⁻¹ which makes it difficult to wet most surfaces without the aid of a surfactant. Silicones have the peculiar property to be able to wet their own adsorbed film. Their liquid surface tension is between 21 mN.m⁻¹ and 22 mN.m⁻¹ whereas the critical surface

\[ \text{Surface Tension of Water} = 72 \text{ mN.m}^{-1} \]

\[ \text{Surface Tension of Silicones} = 21 \text{ to } 22 \text{ mN.m}^{-1} \]

\[ \text{Critical Surface Tension} \]

Figure 1.6: Schematic arrangement of amino-modified silicone softeners on polyester fiber surface (adapted from Schindler et al. [21] figure 3.7)
tension of wetting of a solid silicone film is 24 mM.m$^{-1}$ [24]. Polyester having a critical surface tension of 43 mN.m$^{-1}$, wetting of polyester substrate can be achieved with silicone based formulations.

1.2.3 Role of Si element in flame-retardancy

Silicon (Si) sources employed as flame retardants additives in a polymer system have sometimes provided some conflicting results [25]. However, it is not uncommon to find studies using silica in the composition of nanoparticles suspensions for the treatment of polyester [26].

More generally, this issue has been researched by adding limited quantities of silicon compounds to a variety of polymeric materials [27]. For instance, when using PDMS in flame-retardant formulations, the silica residues provide a shielding effect by acting as an insulating layer [28]. In another study on the flammability properties of poly(butylene terephthalate) containing montmorillonite nanoclays, it was suggested that the nanofillers offered greater resistance to melting [29].

1.3 Combustion

1.3.1 Heat

Heat transfer can occur through several mechanisms that should be differentiated to better identify the consequences of applying a small flame to a material. These mechanisms are listed in Table 1.2. One type of heat transfer, conduction, occurs when a direct contact is established between the heat source and the material. Convection refers to heat being transferred by a fluid, either a liquid or a gas, between the source and the
material. For instance, hot air just above the tip of a flame will heat a material as the flame approaches it. Another type heat transfer is via radiation. In this case, electromagnetic waves convey the energy to the material without the need of fluid as support.

*Table 1.2: Types of heat transports depending upon the medium (adapted from Gié et al. [30])*

<table>
<thead>
<tr>
<th>Medium</th>
<th>Convection</th>
<th>Conduction</th>
<th>Radiation</th>
</tr>
</thead>
<tbody>
<tr>
<td>vacuum</td>
<td>no</td>
<td>no</td>
<td>yes</td>
</tr>
<tr>
<td>solid</td>
<td>no</td>
<td>yes</td>
<td>Yes, if transparent</td>
</tr>
<tr>
<td>fluid</td>
<td>yes</td>
<td>yes</td>
<td>Yes, if transparent</td>
</tr>
</tbody>
</table>

1.3.2 Polymers combustion

Flammability usually refers to the ease of ignition of a material as well as its consequent rapid burning, thus indicating if said material is a fire hazard. However, for flammability to be understood, one must appreciate that it does not refer to a single material property but rather an intricate combination of critical parameters. The burning behavior of a specific material includes the ease of thermal degradation, ease of ignition, rate of flame spread, rate of heat release and ease of extinction [31]. The Oxford English Dictionary defines combustion as “the action or process of burning; consumption or destruction by fire” and as “the development of light and heat accompanying chemical combination” [32]. Distinctions can be made between flaming and smoldering combustion. Smoldering is what is observed in a cigarette, burning slowly and without a
This discussion will focus on flaming phenomena since materials such as thermoplastics which decompose to give liquid products do not smolder [34]. The original viewpoint on the combustion process involves the fire triangle shown in Figure 1.7.

![Fire Triangle Diagram](image)

**Figure 1.7: Simple representation of the “fire triangle”**

In the combustion of polymers, the combustible section is the fuel provided by the volatile parts of the polymer originating from the thermal degradation of the material due to a heat source. However, in order to proceed with the combustion, a combustive (oxidizing) agent is necessary. In this case the combustive part is the oxygen from the air. This gaseous mixture can then be ignited at two different key temperatures. The first threshold occurs when the flash point temperature has been reached. The flash point temperature of a substance is defined as the minimum temperature at which sufficient vapor is produced to form, close to the surface of a combustible fluid, a mixture with air.
which is within the flammability limits [35]. Consequently, at the flash point, the mixture
will ignite if provided with an external source of energy such as a spark or a small
flame. If no external energy source is provided and the temperature keeps rising, the
mixture will spontaneously ignite once it reaches its auto-ignition temperature. It is the
lowest temperature at which the substance will produce hot-flame ignition in air at
atmospheric pressure without applying a spark [35]. At this point, the activation energy of
the combustion reaction is attained [36]. For the combustion to be sustained, enough heat
has to be released from the combustion of the fuel source, so that the combustible keeps
decomposing. Figure 1.8 shows a simplified step by step description of a general
combustion process.
In order to generate volatile fuel species for the burning process to take place, both intermolecular and intramolecular chemical bonds must be broken by supplying enough energy. Several types of depolymerization processes can take place upon thermal degradation. When end-groups are preferentially released from the chain, it is referred as end-chain scission or unzipping. When bonds break at random points along the chain length, the process is called random chain scission. Lastly, if side groups are preferentially released, this process is referred as chain stripping [37].

Figure 1.8: Schematic of simplified combustion process
Different phases can be looked at independently when investigating the physical
and chemical processes occurring in the burning process. The condensed phase of
combustible compounds refers to solids and liquids. The gas phase refers to the gases and
volatile liquids. The mesophase is the interface between the two phases. The kinetics
occurring in the gas phase of the fuel component leading to the burning process can be
divided into seven steps [38]:

1- Initiation: RH → R• + •H

2-Branching: •H + O₂ → •OH + O

3-Propagation (main exothermic reaction): •OH + CO → CO₂ + •H

4- Propagation: •OH + H₂ → H₂O + •H

5-Termination: •H + O₂ → •HO₂

6-Inhibition: •H + HX → H₂ + •X

7-Inhibition: •OH + HX → H₂O + •X

Fuel is shown with R and halogen compounds are shown with X while active
radicals are shown with “•”. The last two steps would be seen in the case of halogen
based flame retardants, acting as radical scavengers.

1.3.3 Flame-retardants

In the textile industry, the main uses of flame-retardants are protective wear,
children's sleepwear, building materials and furnishings, which includes curtain material
and upholstery [39]. They can intervene in different manners in the burning process, by either rendering the ignition virtually impossible, delaying the flame spread, or delaying the time of flashover, thus giving enough time for people to escape [40]. Modes of action of flame retardants are continuously being revised and new ones proposed, making the matter a thriving topic [41]. Basically flame retardants can act either physically or chemically on the burning process. When the combustion process is retarded through a physical action, the flame retardant can do so by cooling, by forming a protective layer or by dilution. If it is a chemical process, it can either react in the gas phase or in the solid phase [37].

A very efficient flame retardant used for polyester fibers was tris-(2,3-dibromopropyl phosphate) (generally known in the industry as “tris” for short). Tris has been banned since 1977 by the U.S Consumer Product Safety Commission (CPSC) because it was considered to be supposedly carcinogenic [42]. Polyester fibers can be flame-retarded using a phosphonate or a hexabromocyclododecane (HBCD) compound in a thermosol process. This process comes from the dyeing industry where the polyester is heated up to 210°C so that the dyes can sublime into the fibers in a short period of time [43]. It is also referred as thermal fixation. However, United Nations countries have agreed to stop using HBCD under Stockholm Convention in 2013 [44].

1.3.4 Combustion of polyester

As a thermoplastic material, once the degradation process is initiated, it produces lower molecular weight components which first melt and then volatilize [45]. Random
chain scission is the main event occurring during the thermal degradation of polyester. This decomposition will mainly form acetaldehyde, carbon monoxide, carbon dioxide and ethane [46]. Table 1.3 lists the main temperature thresholds for PET.

<table>
<thead>
<tr>
<th>Thermal event</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glass transition</td>
<td>80</td>
</tr>
<tr>
<td>Softening/shrinkage</td>
<td>230-250</td>
</tr>
<tr>
<td>Melting point</td>
<td>250</td>
</tr>
<tr>
<td>Pyrolysis</td>
<td>420-447</td>
</tr>
<tr>
<td>Ignition</td>
<td>480-500</td>
</tr>
</tbody>
</table>

Figure 1.9 shows proposed mechanisms for the thermal degradation of PET. In this particular example, these mechanisms refer to pyrolysis in an inert atmosphere, which is different than a flaming combustion in air. In this discussion, the term pyrolysis will refer to a thermal degradation process occurring in the presence of oxygen from the air.
Figure 1.9: Proposed mechanism for the thermal degradation of PET (adapted from Gann et al. [80] Figure 4)
1.3.5 Flammability testing

1.3.5.1 Overview of flammability testing

There are numbers of configurations in which textile materials can be tested for flame resistance. Depending upon the type of product, its end use or its requirements, a substantial number of flammability tests are available in the USA and Canada to assess a material response to heat and flame [49]. In addition, most countries have their own standards, the most common ones being listed in Table 1.4.

One of the most stringent known is the federal flammability standard for children's sleepwear (formerly DOC FF 3-71), now known has CPSC 16 CFR 1616 [50]. In this test, once placed in a vertical configuration, a fabric is first subjected to a bottom ignition for three seconds and the subsequent char length is measured [51].

In a vertical configuration, melting and dripping behavior can greatly influence the flame spread [52]. Charring is often desired since melting and dripping as a mechanism of flame extinguishing is perceived as another fire hazard [53,54]. Molten flaming droplets in conjunction with melting might only result in a pool fire. However, reducing melt dripping can conflict with flame retardancy. The heat generated by the combustion of the samples will not be removed from the system [55].
Table 1.4: Common flammability tests (adapted from Schindler et al. [56] Table 8.4)

<table>
<thead>
<tr>
<th>Test Method</th>
<th>Sponsoring organisation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>16 CFR 1610</td>
<td>Consumer Product Safety Commission (CPSC)</td>
<td>Fabric held at 45° angle to flame for 1 s. For general apparel.</td>
</tr>
<tr>
<td>16 CFR 1615/1616</td>
<td>CSPC</td>
<td>Fabric held vertical to flame for 3 s. For children's sleepwear.</td>
</tr>
<tr>
<td>NFPA 1971</td>
<td>National Firefighters Protection Association (NFPA)</td>
<td>Fabric held vertical to flame for 12 s. For protective clothing.</td>
</tr>
<tr>
<td>NFPA 701</td>
<td>NFPA</td>
<td>Fabric held vertical to flame for 45 s to 2 min. For drapery.</td>
</tr>
<tr>
<td>ASTM D-2863 Limiting oxygen Index (LOI)</td>
<td>American Society for Testing and Materials (ASTM)</td>
<td>Fabric is held vertical in atmosphere of different oxygen/nitrogen ratios and ignited from top. Determines minimum oxygen level to support combustion.</td>
</tr>
<tr>
<td>BS 5852 Part 1 and 2, for ignition sources 'cigarette' and 'match' equivalent also EN 1021 and EN 597</td>
<td>British Standards Institution (BSI)</td>
<td>Burning behavior of upholstered furniture fabrics (also for private use) against smoker-materials like cigarettes and matches. Finished fabric must be soaking resistant at 40°C according to BS 5651, then horizontally and vertically fixed on a mini chair on a support of foamed PU, by seven ignition methods.</td>
</tr>
<tr>
<td>ISO 6940/6941</td>
<td>International Organization for Standardization (ISO)</td>
<td>Vertically held specimens, determination of the ease of ignition/the flame spread properties.</td>
</tr>
<tr>
<td>DIN 54333 T1</td>
<td>Deutsches Institut für Normung (DIN)</td>
<td>Horizontally held specimens, because of the heat distribution less severe than vertical tests</td>
</tr>
</tbody>
</table>
1.3.5.2 Influence of fiber morphology on burn tests

During the melt spinning process of polyester, the drawing process above its glass transition temperature gives polyester filaments molecular orientation and extension as shown in Figure 1.10 [57]. During the drawing step, chain segments in the amorphous region are oriented along the fiber longitudinal introducing elastic as well as plastic deformation in the fiber [58]. The extension is conserved by the plastic deformation, putting the elastically deformed non-crystalline region under stress [59]. Consequently, when the temperature of the fiber is increased by applying heat, the thermodynamically driven behavior and the softening of the fiber allow the amorphous regions to reach their natural coiled configuration. This can be regarded as the heated extended rubber band experiment as the disordered state is entropically favorable whereas oriented regions have lower entropy [60]. Thus if the temperature is high enough, the fabric will shrink away.

Figure 1.10: Structural model of oriented semicrystalline PET (adapted from Göschel [101] Figure 16)
1.4 Flammability issues

1.4.1 Polyester

PET fibers may be considered less flammable than cellulosic fibers as their natural propensity is to melt and shrink away before they can ignite [5]. Therefore, some misconceptions may arise when discussing the burning behavior of PET. For instance, if cotton is considered readily flammable, polyester would be moderately flammable whereas wool would be considered as relatively nonflammable. Many different factors related to the fabric properties can affect textile flammability, such as fiber content, yarn twist, fabric construction, fabric density, fabric weight and fabric finishes. In Canada, the minister of Health recommends to treat finishes which are not specifically designed as flame retardants as an unknown variable [61].

The usual performance of a 100 percent polyester fabric is to drip when tested for flammability, thus gaining the qualification of “self-extinguishing” once the flame has been removed. In its fire safety checklist the U.S. Consumer Product Safety Commission recommends to look for fabrics made predominantly from thermoplastics fibers such as nylon, polyester, acrylic, and olefins when selecting upholstered furniture because they resist ignition better than cellulosic fabrics. This recommendation also follows for apparel section where it is recommended to use fabrics such as 100 percent polyester, nylon, wool and silk that are difficult to ignite and tend to self extinguish. It is also recommended that cotton/polyester blends should be avoided [62]. However, this does not mean that 100% polyester fabrics are non-flammable. For example, tags on fiberfill
products, read “This article meets the flammability requirements of California Bureau of Home Furnishings Technical Bulletin 117. Care should be exercised near open flame or with burning cigarettes.”

The fact that a product passes a specific standard does not necessarily mean that it will not fail in another configuration or that it is absolutely flame proof. This kind of discrepancy resulted in the development of a new flammability test method for aircraft blankets by the Federal Aviation Administration (FAA) after a fire in an overhead stowage bin was attributed to 100 percent polyester airline blankets [63]. In this example, even though a non-FR treated 100 percent polyester blanket passed a vertical flame test, it would consistently fail a 4-ply horizontal flame test. Furthermore, in 2004 the National Association of State Fire Marshals (NASFM) stated that the existing federal general wearing apparel standard does not protect consumers from clothing fires [64]. It referred to the Standard for the Flammability of Clothing Textiles, 16 CFR Part 1610, which may mislead customers by characterizing a specimen as “does not ignite” when in many real situations it would ignite.

1.4.2 Perception on the effect of silicone finishes on the burning behavior of PET

Polyester fiberfill has proven to be challenging when dealing with flame retardancy. Even though a component might pass a flame test, the assembled furniture could still fail. Several patents acknowledge the need for a more stringent component. For instance, in the United States Patent number 4,040,371 “Polysiloxane coated polyester fibers blended with other fibers to obtain fibrous mass having more acceptable
flame resistance than a mass of unblended polysiloxane coated fibers”, the title itself shows the problems caused by the PDMS-coated PET fibers on flammability [65]. Later, the same inventors mention again the improvements felt necessary in order to improve the horizontal burning rate of silicone coated polyester fiberfill when subjected to a small flame in patent number 4,199,642 [66].

Patent number 4,054,695 relates to compositions of chelating agents for treating silicone-treated polyester fibers and thus improve their flame retardancy, pointing out the fact that “in many instances the silicones tend to cause a deterioration in flammability, particularly when the synthetic is a polyester fiber” [67].

In 2008, the NASFM mentioned their concerns concerning a proposed new rule for upholstered furniture which the Science Advisory Committee (SAC) calls “grossly deficient in two instances: its failure to address ignitions by small open flame, and its failure to protect against ignition of filling materials.” This uneasiness over filling material is justified since the filling materials are the main source of fuel of upholstered items. Once more it is stated that there are “materials located directly beneath the cover fabric, that are even more highly flammable than the standard polyurethane foam substrate specified in the test” – examples are loose-fill shredded polyurethane cushioning and what is know as “slickened” polyester fiber [68]. Clearly silicone based coatings for polyester fibers are negatively perceived in the industry in terms of burning behavior.

Even with an inherently low-flammability polyester fiber such as Trevira CS®,
caution is advised. In his paper, Mach rules out silicone-based softeners in pigment printing because of their detrimental influence on the burning behavior of textiles [69]. In another investigation on the influence of silicone-treated components, Sanders looked at the effect of seaming thread lubricants on flammability performance of polyester fabrics [70]. It was concluded that silicone-lubricated threads increased the residual flame time in seamed polyester fabrics. More specifically, the average residual flame time between a non silicone lubricant and a silicone one went from 3.6 seconds to 30 seconds in that specific vertical configuration. In a technical bulletin American & Efird, Inc (A&E) announced the development of two polyester threads that had a special non-silicone finish commonly used in children's sleepwear so that a designed garment could pass the flammability seam testing requirements [71]. Indirectly, A&E acknowledges the negative effect of silicone coated polyester threads on the burning behavior of a fabric. However, it states that fabrics that have “good flame retardant properties can be sewn with regular spun polyester with a silicone lube and generally pass the flammability tests” (i.e. fabric treated with flame retardants). When reviewing common flame retardants in use for thermoplastic polyesters, Weil states that when the mode of action of flame retardants seems to be mainly melt-flow enhancement, if the flow is impeded by solids, the flame retardancy is badly compromised [72]. Once again it is recommended that silicone spinning lubricants must be avoided. Weil, in a later review, describes the effect of silicones as making the polyester more “flammable by traces of silicones which probably burn to silica and then act as wick” [73].
In the textile domain, the effect of silicone finishes on the burning behavior of polyester was first questioned in the 1970s when they were shown to interact with polyester fibers in both physical and chemical mechanisms. It was stated that despite the thermal stability of silicones, they seemed to increase the flammability of polyester fibers. This may appear counterintuitive since silicones are also used as part of flame retardant formulations with several other polymers. Consequently, a specific system needs to be established along with a well defined nomenclature when in order to avoid any confusion with work in the development of flame retardants for instance.

1.4.3 Theories on the effect of silicone finishes on the burning behavior of PET

Several mechanisms were proposed as to why and how a silicone-treated (sometimes referred as slickened) polyester fibers would behave differently to untreated polyester fibers when subjected to a flame. In one experiment Swihart and Campbell treated carpet yarn made out of Kodel II polyester fibers with a 100 ppm Dow Corning antifoam silicone fluid emulsion [74]. Even at such a low level, the melting behavior, the burning behavior as well the thermal stability of the silicone-treated Kodel II fibers were negatively altered in a significant way.

The first theory explaining this modified burning mechanism of polyester fiber relies on a physical process. The inherent behavior of polyester fibers when submitted to a flame is to melt and shrink away from the flame. However, once the fibers have been silicone treated, this contraction does not occur because of the reduction of the surface energy of the fibers. This explanation is relevant in a vertical flame test configuration
where the polyester will flow freely into the heat source instead of shrinking away.

Another hypothesis deals with the reduction of the melt viscosity due to the rapid depolymerization of the polyester substrate. In this proposed interaction, the oxidation of the silicone results into the formation of silanol which will then react with the ester linkage in the polyester polymer chain. This reaction is presented in Figure 1.11. In the reaction, a carboxy-terminated polyester is formed and increases the rate of depolymerization. In a vertical flame test configuration, this can affect both the polymer flow in the flame and increase the rate of volatilization of flammable products.

Another possibility in the burning behavior of silicone-treated polyester fibers refers to what is called the “scaffold effect”. When dealing with the flame retardancy of polyester cotton blends, studies always mention this deleterious effect encountered during the burning process. Once the polyester starts to melt, instead of shrinking away it melts on the charred cotton thus staying in the combustion process.

In a later experiment, Swihart investigated how silicone softeners affected the burning behavior of flame retarded cotton and polyester/cotton fabric on a mannequin [75]. It was concluded that the softeners had no deleterious effect on non-flame retarded samples compared to non-silicone treated non-flame retarded samples. Moreover, their
effect on flame retarded samples would vary from lowering the flame resistance to no noticeable difference.

1.5 **Aim of research**

The goal of this research is first to determine if the perception of the industry over the effect of silicone finishes on the burning behavior of polyester is based on reproducible experiments or only on anecdotal events. The statement that using silicone-treated polyester fibers in fiberfill applications increases the flammability of the overall component has first to be verified under controlled conditions. A preliminary assessment of the burning behavior of a silicone-treated polyester fiberfill-like substrate will be conducted using a 45° angle flame test. Once any detrimental pattern is established, the research will attempt to determine the mechanisms with which the burning behavior of silicone-treated polyester materials proceeds.

In order to create a reproducible setup of the burning process, a substrate representative of polyester fiberfill will be used. Some restrictions are to be imposed since the substrate needs to be uniform in terms of fiber distribution and it needs to retain its physical integrity as well as its dimensions after wet treatments. Finally, it needs to be free of uncontrolled treatments or finish. To satisfy the conditions previously stated, a spunbond needled polyester nonwoven substrate will be chosen.

This research will select a wide array of silicone-based finishes, however it will not attempt to define the exact formulations of these finishes. Most of these compounds have a proprietary formulation and the goal here is not to perform reverse-engineering on
commercially available softeners. Nonetheless, the effect of functionality will be investigated based on the end use and description of specific finishes. In addition, the effect of the heat treatment used in the curing process will also be studied. Finally, the amount of finish used to treat the polyester materials will be monitored in an attempt to establish a limit under which the inherent burning behavior of polyester would not be disrupted.

The burning behavior will be researched using a standard vertical flammability test employed in the industry. The parameters of interest are the percentages of mass and area loss after a flame test as well as the duration of the flame during the tests. In a consumer oriented context, these tests are designed as pass or fail, focusing on the time component. In this study, the results obtained from these tests are used as relative values in order to compare specific treatments.

The thermal degradation of treated polyester fibers will also be scrutinized in an effort to compare decomposition rates. Residues will be analyzed to show if any unexpected chemical or physical interactions occurred. Through these techniques, a more accurate description of the effect of silicone finishes on the burning behavior of polyester will be provided.
CHAPTER 2
EXPERIMENTAL

2.1 Materials

Table 2.1: List of chemicals used in substrate treatments

<table>
<thead>
<tr>
<th>Chemical name</th>
<th>Supplier</th>
<th>Shortened name used in text</th>
</tr>
</thead>
<tbody>
<tr>
<td>Powersoft® CF 20</td>
<td>Wacker Silicones</td>
<td>Powersoft</td>
</tr>
<tr>
<td>Emulsion AF-2340</td>
<td>Wacker Silicones</td>
<td>AF2340</td>
</tr>
<tr>
<td>Wetsoft® CTA</td>
<td>Wacker Silicones</td>
<td>Wetsoft</td>
</tr>
<tr>
<td>SE-26</td>
<td>Wacker Silicones</td>
<td>SE26</td>
</tr>
<tr>
<td>CT 205E</td>
<td>Wacker Silicones</td>
<td>CT205E</td>
</tr>
<tr>
<td>R1016 Lurol PS-662</td>
<td>Goulston Technologies</td>
<td>PDMS A</td>
</tr>
<tr>
<td>R0992 Lurol PS-11158-50%</td>
<td>Goulston Technologies</td>
<td>PDMS B</td>
</tr>
<tr>
<td>Silicone Fluid with curing agent</td>
<td>Goulston Technologies</td>
<td>SFC</td>
</tr>
<tr>
<td>Reapret® SR New</td>
<td>Giovanni Bozetto S.p.A</td>
<td>SR</td>
</tr>
<tr>
<td>Triton X-114</td>
<td>Sigma-Aldrich</td>
<td>Triton</td>
</tr>
<tr>
<td>Pluronic 17R2</td>
<td>BASF</td>
<td>Pluronic</td>
</tr>
<tr>
<td>Sodium Silicate, Na$_2$SiO$_3$, 5H$_2$O</td>
<td>Sigma-Aldrich</td>
<td>Sodium Silicate</td>
</tr>
<tr>
<td>Hexane, 98.5%</td>
<td>VWR</td>
<td>N/A</td>
</tr>
</tbody>
</table>

Table 2.1 lists the different chemicals used in the PET treatment processes and Table 2.2 describe the available information concerning the functionalities of specific silicones commercially available. It should be noted that the two surfactants Triton X-114 and Pluronic 17R2 listed above were not used as part of standard silicone-based treatment formulations but used in a separate treatment without any silicone finishes.
<table>
<thead>
<tr>
<th>Name</th>
<th>Description</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Powersoft</td>
<td>Self-crosslinking and amino functional elastomeric silicone softener micro emulsion with 20% total solids with approximately 14% of active contents</td>
<td>poly[3-((2-aminoethyl)amino)propyl]methyl (dimethyl) siloxane, hydroxyl-terminated and octamethyl cyclotetrasiloxane</td>
</tr>
<tr>
<td>AF2340</td>
<td>40% general purpose silicone softener micro emulsion using a high molecular weight amino fluid</td>
<td>diethyleneeglycol monobutyl ether, aminofunctional polydimethylsiloxane and octamethyl cyclotetrasiloxane.</td>
</tr>
<tr>
<td>Wetsoft</td>
<td>self dispersable amino functional hydrophilic silicone softener</td>
<td>polydimethylsiloxane with aminoalkyl and polyether groups.</td>
</tr>
<tr>
<td>SE26</td>
<td>a silicone antifoam emulsion, based on a high molecular weight polysiloxane and silica technology</td>
<td>an emulsion in water of polydimethylsiloxane and a filler.</td>
</tr>
<tr>
<td>CT205E</td>
<td>silicone emulsion for textile fiber finish, containing polydimethylsiloxane with functional groups</td>
<td>alpha-iso-tridecyl-omega-hydroxypolyglycolether and poly[3-((2-aminoethyl)amino)propyl]methyl (dimethyl) siloxane, hydroxy-terminated</td>
</tr>
<tr>
<td>PDMS A</td>
<td>dimethylpolysiloxane fluid with a viscosity of 1000 cSt.</td>
<td>Proprietary blend</td>
</tr>
<tr>
<td>PDMS B</td>
<td>dimethylpolysiloxane fluid with a viscosity of 350 cSt</td>
<td>Proprietary blend</td>
</tr>
<tr>
<td>SFC</td>
<td>Emulsion with curing agent, 50% solids</td>
<td>95% silicones, 5% curing agent</td>
</tr>
<tr>
<td>SR</td>
<td>antistatic and soil release durable finishing agent for polyester fibers and blends</td>
<td>poly(oxyethylene) terephthalate polymer, Stearylimidazoline, Water</td>
</tr>
<tr>
<td>Pluronic</td>
<td>A nonionic surfactant that is 100% active and relatively nontoxic</td>
<td>Difunctional block copolymer surfactant with terminal secondary hydroxyl groups</td>
</tr>
<tr>
<td>Triton</td>
<td>nonionic detergent produced from octylphenol polymerized with ethylene oxide, supplied as a 100% detergent preparation</td>
<td>Polyethylene glycol tert-octylphenyl ether</td>
</tr>
</tbody>
</table>
2.2 Useful equations in finish applications

In a batch process, the quantity of finish to apply to a substrate can be expressed as a weight percentage based on the untreated fabric weight [76]. That amount is referred as on weight of fabric (% owf) or on weight of goods (% owg).

\[
% \text{ owf} = \frac{\text{mass of finish applied}}{\text{mass of fabric before treatment}} \times 100
\]  \hspace{1cm} (5)

The values obtained through equation (5) do not represent the final weight of finish on the fabric. The mass of finish applied in equation (5) refers to the mass of the commercial product used, not the mass of solid contents. Thus the add-on percent is calculated in equation (6) by weighing the dry fabric after treatment [77]. Fabric samples were conditioned for 24 hours before each weighing.

\[
% \text{ add-on} = \frac{\text{mass of fabric after drying} - \text{mass of fabric before treatment}}{\text{mass of fabric before treatment}} \times 100
\]  \hspace{1cm} (6)

The % add-on value allows one to compare treated samples based on the actual amount of finish present on the substrate whereas the % owf value is measured at the beginning of the fabric treatment process. Figure 2.1 illustrates the difference between the two values.

---

**Figure 2.1: Flowchart of % owf and % add-on relationship**
2.3 Initial examination of the effect of silicone finishes on the burning behavior of PET

2.3.1 Effect of silicone finishes on the burning behavior of a “lofty” needlepunched polyester fabric

2.3.1.1 Description of the polyester substrate used during the initial examination

In this preliminary study, a “lofty” nonwoven fabric was assembled using 6 denier 2 inch length polyester staple fibers. The fibers were processed in a continuous needle punch line, where they were first opened in a Rando opener which feeds the fibers into a chute system, leading to a 20 inch Befama card. The web was then processed through a 24 inch Automatex cross lapper conveyor system before passing through a 27 inch wide Automatex needle loom, containing a total of 1376 needles. The machine was set on 100 strokes/min with a needle depth of 0.7 inch, making a fabric of 270 g.m⁻².

2.3.1.2 Treatments carried on the “lofty” polyester substrate during the initial examination

Finish CT205E was applied at the levels listed in Table 2.3 following a uniform spraying pattern as shown in Figure 2.2 after being dispersed in 100mL of deionized water. This spraying method used nitrogen as the propulsion gas. The fabric was sprayed on both sides. The fabric was air dried and half of the samples were cured for 10 minutes at 170°C. Finish SFC was applied in the same fashion.
Table 2.3: List of “lofty” needlepunched substrate treatments

<table>
<thead>
<tr>
<th>Finish treatment</th>
<th>% add-on</th>
<th>Heat treatment 170°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>CT205E</td>
<td>0.1%</td>
<td>1%</td>
</tr>
<tr>
<td>CT205E</td>
<td>0.1%</td>
<td>1%</td>
</tr>
<tr>
<td>SFC</td>
<td>2%</td>
<td>0 min</td>
</tr>
</tbody>
</table>

2.3.1.3 Burning behavior of the “lofty” needlepunched nonwoven polyester substrate

During this initial examination, a flame test was performed on the polyester substrate using standard test method for flammability of apparel textiles ASTM D1230-10 [78]. The samples were cut using a 2” by 6” die on a USM hydraulic press. A dried specimen was inserted in a frame as shown in Figure 2.3 and inserted in the Atlas AFC auto flame chamber at an angle of 45° as seen in Figure 2.4. This test will be referred as “diagonal flame test” due to the geometric configuration. A standardized CP grade butane flame was then applied to the surface of the sample near the lower end for 5 s. The flame-spread time required for the flame to proceed up the fabric a distance of 5”
was recorded. If the flame did not reach that point, no value was recorded. Particular attention was paid to the melt drip behavior. The mass of the sample after burning was then recorded on a Mettler AE200 balance.

![Figure 2.3: Schematic of sample holder for diagonal flame test](image)

For each type of treatment, five samples were submitted to the diagonal flame test. Figure 2.5 is a summary of the different batches submitted to a diagonal flame test. In addition, a control batch of untreated fabric was subjected to the flame test previously described.
Figure 2.4: Side view schematic of sample position in flame chamber

Figure 2.5: Summary of preliminary study of burning behavior
2.3.1.4 Fourier Transform Infrared (FTIR) analysis

FTIR analysis was performed using a Magna-IR Spectrometer 550 Nicolet, coupled to a Foundation Series Diamond ATR (Attenuated Total Reflectance) by Thermo Spectra Tech. Figure 2.6 shows how the sample is mounted on the crystal, where the IR beam penetrates only a few micrometers into the sample [79]. The needlepunched fabric was analyzed before and after treatment with finish CT205E. Samples were 2” by 6” with the instrument set on 16 scans per analysis.

![Figure 2.6: Schematic of horizontal ATR contact sampling technique (adapted from Martin-Gil et al. [99])](image)

2.3.2 Effect of silicone finishes on the burning behavior of spunbond needled polyester fabric

2.3.2.1 Description of spunbond needled polyester nonwoven substrate

In this second part of the preliminary study, the substrate was switched to a spunbond needled nonwoven of 140 g.m$^{-2}$ of 4 denier polyester fibers. The fabric thickness was 0.96 mm, using an AMES digital thickness gauge.
2.3.2.2 Treatments carried on spunbond needled polyester nonwoven substrate

Samples of fabric were hand cut from the spunbond fabric roll to a size of 8” by 11”. Silicone finishes PDMS A and PDMS B were dissolved in 100 mL of hexane to obtain the % owf listed in Table 2.4. The procedure was repeated for Reapret® SR New (non silicone-based finish) with water. The fabric was soaked flat in dish in the 100 mL solution and left flat to dry until all the solvent evaporated.

Table 2.4: List of PET spunbond substrate treatments

<table>
<thead>
<tr>
<th>Finish treatment</th>
<th>% owf</th>
<th>Solvent</th>
</tr>
</thead>
<tbody>
<tr>
<td>PDMS A</td>
<td>6.25%</td>
<td>12.5%</td>
</tr>
<tr>
<td>PDMS B</td>
<td>6.25%</td>
<td>12.5%</td>
</tr>
<tr>
<td>SR</td>
<td>6.25%</td>
<td>25%</td>
</tr>
</tbody>
</table>

2.3.2.3 Burning behavior of spunbond needled polyester nonwoven substrate

For each batch of treated fabric listed in Table 2.4, 5 samples were cut using a 2” by 6” die and a USM hydraulic press. The diagonal flame test procedure described in section 2.3.1.3 (see page 33) was applied to these samples as well as five samples of untreated PET substrate.

2.3.2.4 FTIR

Using the same apparatus described in 2.3.1.4 treated samples were analyzed to compare absorbance to level of treatment. Each sample was analyzed on three different spots on each side on the fabric.
2.4 Central investigation into the effect of silicone finishes on the burning behavior of PET

2.4.1 Description of substrates used during the central investigation

Two substrates were used to investigate the effect of silicone finishes on the burning behavior of polyester during the central investigation: a manufactured spunbond needled nonwoven (described in section 2.3.2.1, see page 36) as well as a polyethylene terephthalate biaxially oriented film from Goodfellow. Table 2.5 and Table 2.6 below list the specifications of each substrates.

Table 2.5: PET spunbond nonwoven roll specifications

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Width</td>
<td>14”</td>
</tr>
<tr>
<td>Thickness</td>
<td>0.96 mm</td>
</tr>
<tr>
<td>Basis weight</td>
<td>140 g.m⁻²</td>
</tr>
</tbody>
</table>

Table 2.6: PET film roll specifications

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Length</td>
<td>20 m</td>
</tr>
<tr>
<td>Width</td>
<td>300 mm</td>
</tr>
<tr>
<td>Thickness</td>
<td>0.023 mm</td>
</tr>
<tr>
<td>Mass of total roll</td>
<td>192 g</td>
</tr>
</tbody>
</table>

2.4.2 Treatments carried on polyester substrates

2.4.2.1 Treatments carried on spunbond needled polyester nonwoven substrates

Samples were cut from the spunbond fabric roll to a size of 3” by 12” and weighed. Finishes were first dispersed in hexane or water to obtained the desired % owf based on the fabric mass. For each batch, 3 fabric samples were placed in a Pyrex® dish, soaked in the 100mL solution prepared and left until all the water or hexane evaporated.
This method was repeated twice to prepare 6 samples per finish per % owf. The treatments applied are listed in Table 2.7.

Table 2.7: List of treatments applied to spunbond fabric for vertical flame test

<table>
<thead>
<tr>
<th>Finish</th>
<th>% owf</th>
<th>Solvent</th>
</tr>
</thead>
<tbody>
<tr>
<td>PDMS A</td>
<td>0.1%</td>
<td>1%</td>
</tr>
<tr>
<td>PDMS B</td>
<td>0.1%</td>
<td>1%</td>
</tr>
<tr>
<td>CT205E</td>
<td>0.1%</td>
<td>1%</td>
</tr>
<tr>
<td>SE26</td>
<td>0.1%</td>
<td>1%</td>
</tr>
<tr>
<td>Powersoft</td>
<td>0.1%</td>
<td>1%</td>
</tr>
<tr>
<td>Wetsoft</td>
<td>0.1%</td>
<td>1%</td>
</tr>
<tr>
<td>AF2340</td>
<td>0.1%</td>
<td>1%</td>
</tr>
<tr>
<td>SR</td>
<td>0.1%</td>
<td>1%</td>
</tr>
<tr>
<td>Triton</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pluronic</td>
<td></td>
<td>10%</td>
</tr>
<tr>
<td>Sodium silicate</td>
<td>0.1%</td>
<td></td>
</tr>
</tbody>
</table>
2.4.2.2 *Treatment of polyester film substrate*

Samples were cut from the polyester film roll with a razor blade to a size of 3” by 12”. One layer of a 3” by 12” polyester film sample was spread with approximately 5mL of finish and then covered with a second film as shown in Figure 2.8. A casting blade of thickness 3 mil, (0.003 inches or 76.2 microns) was applied over this “sandwich” configuration in order to remove any excess finish and air bubbles, thus making a uniform coating between the two layers of film. For each finish, 6 samples were made.

![Figure 2.8: Schematic of PET film treatment](image)

2.4.3 *Burning behavior of polyester substrates in vertical flame test*

Flame tests were performed in the VFC Vertical Flame Chamber from Atlas, using the standard test method for flame resistance of textiles ASTM D6413-08 [80]. Samples were weighed before being mounted in a frame and then placed in the flame chamber. The methane (C.P. grade) burner flame was adjusted to a height of 1.5” and the specimen set to 0.75” above the burner as shown in Figures 2.9 and 2.10. The bottom of the specimen was exposed to the flame for 12 s at which point it was observed for melting and dripping behavior. The after-flame time, the length of time for which a material continues to flame after the ignition source has been removed, was recorded. Any afterglow time was recorded. Once removed from the vertical flame chamber, each sample was photographed using a Canon EOS 40D digital camera mounted with a Canon
EF 50mm f/1.8 II lens. Finally the mass of the sample after testing was recorded on a Sartorius balance BP221S. Each treatment category listed in Table 2.8 was tested 5 times.

Table 2.8: Summary of samples submitted to vertical flame test

<table>
<thead>
<tr>
<th>Finish</th>
<th>Treatment</th>
<th>Substrate</th>
</tr>
</thead>
<tbody>
<tr>
<td>PDMS A</td>
<td>0.1%</td>
<td>1%</td>
</tr>
<tr>
<td>PDMS B</td>
<td>0.1%</td>
<td>1%</td>
</tr>
<tr>
<td>CT205E</td>
<td>0.1%</td>
<td>1%</td>
</tr>
<tr>
<td>SE26</td>
<td>0.1%</td>
<td>1%</td>
</tr>
<tr>
<td>Powersoft</td>
<td>0.1%</td>
<td>1%</td>
</tr>
<tr>
<td>Wetsoft</td>
<td>0.1%</td>
<td>1%</td>
</tr>
<tr>
<td>AF2340</td>
<td>0.1%</td>
<td>1%</td>
</tr>
<tr>
<td>SR</td>
<td>0.1%</td>
<td>1%</td>
</tr>
<tr>
<td>Triton</td>
<td></td>
<td>10%</td>
</tr>
<tr>
<td>Pluronic</td>
<td></td>
<td>10%</td>
</tr>
<tr>
<td>Sodium silicate</td>
<td></td>
<td>0.1%</td>
</tr>
<tr>
<td>PDMS A</td>
<td></td>
<td>N/A</td>
</tr>
<tr>
<td>PDMS B</td>
<td></td>
<td>N/A</td>
</tr>
<tr>
<td>CT205E</td>
<td></td>
<td>N/A</td>
</tr>
<tr>
<td>SE26</td>
<td></td>
<td>N/A</td>
</tr>
<tr>
<td>Powersoft</td>
<td></td>
<td>N/A</td>
</tr>
<tr>
<td>Wetsoft</td>
<td></td>
<td>N/A</td>
</tr>
<tr>
<td>AF2340</td>
<td></td>
<td>N/A</td>
</tr>
<tr>
<td>SR</td>
<td></td>
<td>N/A</td>
</tr>
<tr>
<td>N/A</td>
<td></td>
<td>N/A</td>
</tr>
<tr>
<td>N/A</td>
<td></td>
<td>N/A</td>
</tr>
</tbody>
</table>
Figure 2.9: Schematic of burner used in standard vertical flame test

Figure 2.10: Schematic of sample mounted in frame for standard vertical flame test
2.4.4 Photographic analysis

From the photographs taken after the vertical flame testing referred in section 2.4.3 (see page 40), the area loss was measured using ImageJ Software (image processing and analysis in Java) as shown in Figures 2.11 and 2.12 below. The percentage of area loss was then computed based on the area of the fabric within the frame available to the flame.

![Screen capture of scale setting in ImageJ software](image)

*Figure 2.11: Screen capture of scale setting in ImageJ software*
2.4.5 Thermogravimetric analysis

Thermogravimetric analysis was performed using TGA Q5000 from TA Instrument. Runs were conducted in air at the rate of 100 °C.min\(^{-1}\) until a temperature of 1000 °C was reached. For each sample the chamber was purged for 10 minutes with air at a flow rate of 25 mL.min\(^{-1}\) before starting the test. In order to minimize the loss of
residues, fan air cooling was disabled at the end of the test. After cooling down, residue from the TGA pan was collected and transferred on a SEM stub covered with carbon tape. Table 2.9 lists the thermal analyses performed on the substrates and the finishes.

Treated samples were cut from the nonwoven polyester samples as well as from the polyester film samples, to fit the size of the TGA pan, making them approximately 4 mg. The pan was lined with platinum foil to prevent any agglomeration of the thermal degradation by products as well as fusion of residues to the bottom of the pan. After each thermal set, the foil was brushed with a Kimwipe, washed with methanol and the pan was then placed in the flame of butane burner for 30 s to ensure no contamination occurred between samples. Data from the TGA analysis was processed using Universal Analysis 2000 software.

2.4.6 Electron Microscopy

A Hitachi SU 6600 scanning electron microscope was used to observe treated polyester spunbond substrate before and after thermal degradation. For control, untreated polyester fibers from the spunbond fabric were observed as well. Samples were deposited on stubs covered with carbon tape and a piece of copper tape. Variable pressure and the back scattered electron attachment were used. The gaseous environment allows poorly conducting samples to be imaged in a stable manner at any desired beam energy without the need to coat them with a conductive metal layer [81]. A medium probe current was used with an aperture of 14 at a working distance of 10 mm with a pressure of 20 Pa. Images were processed with Quartz PCI software.
### Table 2.9: Summary of thermal analyses

<table>
<thead>
<tr>
<th>Finish</th>
<th>% owf</th>
<th>Substrate</th>
<th>Medium</th>
<th>Heating rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>PDMS A</td>
<td>1%</td>
<td>5%</td>
<td>10%</td>
<td>50%</td>
</tr>
<tr>
<td>PDMS B</td>
<td>1%</td>
<td>5%</td>
<td>10%</td>
<td>50%</td>
</tr>
<tr>
<td>Powersoft</td>
<td>1%</td>
<td>5%</td>
<td>10%</td>
<td>50%</td>
</tr>
<tr>
<td>Wetsoft</td>
<td>1%</td>
<td>5%</td>
<td>10%</td>
<td>50%</td>
</tr>
<tr>
<td>AF2340</td>
<td>1%</td>
<td>5%</td>
<td>10%</td>
<td>50%</td>
</tr>
<tr>
<td>CT205E</td>
<td>1%</td>
<td>5%</td>
<td>10%</td>
<td>50%</td>
</tr>
<tr>
<td>SE26</td>
<td>1%</td>
<td>5%</td>
<td>10%</td>
<td>50%</td>
</tr>
<tr>
<td>SR</td>
<td>1%</td>
<td>5%</td>
<td>10%</td>
<td>50%</td>
</tr>
</tbody>
</table>

N/A

<table>
<thead>
<tr>
<th>Finish</th>
<th>% owf</th>
<th>Substrate</th>
<th>Medium</th>
<th>Heating rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>PDMS A</td>
<td>N/A</td>
<td>PET spinbond fabric</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>PDMS B</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>Powersoft</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>Wetsoft</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>AF2340</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>CT205E</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>SE26</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>SR</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
</tbody>
</table>
2.4.7 Elemental analysis

Elemental analysis was performed using energy dispersive X-Ray Spectroscopy (EDX). Calibration was made with the copper tape and process time set on 6 for a higher resolution. Samples were characterized using Point&ID settings of the Oxford Instruments INCA 4.15 software. Elements were quantified and normalized from the acquired spectra using the “all elements analyzed” option. Elements investigated were carbon, oxygen, silicon, titanium and antimony with results obtained in weight % as well as atomic %. It was performed on the TGA residues of the spunbond fabric coated with finishes obtained in the thermal degradations described in section 2.4.5 (see page 44). For control, it was also performed on the plain spunbond fabric as well as the plain polyester film.

Elemental analysis was also performed on the finishes PDMS A, PDMS B, Powersoft, AF2340, CT205E, SE26 and SR New using the SEM cryo-stage. The sample holder was frozen using liquid nitrogen, a drop of finish was then deposited in the stub and the sample holder was quickly inserted in the exchange area. The stage was held at -18°C during the analysis.

2.4.8 Accelerated solvent extraction

Accelerated solvent extraction (ASE) was performed using a Dionex ASE 200 Accelerated Solvent Extractor on three samples from the untreated spunbond needled polyester nonwoven roll to verify the absence of spin finish. The extraction conditions are listed in Table 2.10 below.
**Table 2.10: Extraction conditions – Dionex ASE extractor**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Specification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure</td>
<td>1500 psi</td>
</tr>
<tr>
<td>Temperature</td>
<td>50°C</td>
</tr>
<tr>
<td>Solvent</td>
<td>Hexane</td>
</tr>
<tr>
<td>Time</td>
<td>5 min heat, 10 min static</td>
</tr>
<tr>
<td>Flush</td>
<td>60% of extraction cell volume</td>
</tr>
<tr>
<td>Purge</td>
<td>60 sec with nitrogen</td>
</tr>
</tbody>
</table>
CHAPTER 3
RESULTS & DISCUSSION

3.1 Initial examination of the effect of silicone finishes on the burning behavior of PET

The preliminary study was conducted to determine if the treatment of a polyester fabric with a silicone-based finish had indeed an effect on the burning behavior of polyester in a standard flammability test. In this initial part of the study, all flame tests are performed using the standard test method for apparel textiles (ASTM D1230-10) described in section 2.3.1.3 (see page 33). It is referred to as diagonal flame test here since the test is conducted at a 45° angle.

Data such as % mass loss and flame-spread times obtained from the diagonal flame test are used to compare the effect of silicone finishes on the burning behavior of a polyester substrate. Comparisons will also be possible using photographic evidence.

3.1.1 Corrected mass loss calculation for diagonal flame test

A normalized mass loss was computed in order to obtain more accurate values than a simple comparison between the mass of the fabric before and after the diagonal flame test.

\[
\%\text{uncorrected mass loss} = \left(\frac{M_{bd} - M_{ad}}{M_{bd}}\right) \times 100
\]

Where

\(M_{bd}=\text{Mass of sample before diagonal flame test}\)
\( M_{ad} = \text{Mass of sample after diagonal flame test} \)

As shown in Figure 2.3, only part of the total width of the sample can be subjected to the flame during the test and Equation (7) would not reflect the true \% mass loss. If we assume that the frame is a rectangle exactly conformed to the standard specifications and that the substrate has a uniform weight, we can consider that only 1.5” out of 2” of the sample width is available to be consumed by the flame. Since the whole length of the sample fits within the frame, we can postulate that one fourth of the sample is protected by the frame, thus unavailable for testing.

\[
\% \text{ corrected mass loss} = \frac{M_{bd} - M_{ad}}{M_{bd}} \times 100
\]  
(8)

Where

\[
M_{bd}' = M_{bd} - \frac{1}{4} \times M_{bd}
\]  
(9)

\[
M_{ad}' = M_{ad} - \frac{1}{4} \times M_{bd}
\]  
(10)

Inserting equations (9) and (10) into equation (8) gives us

\[
\% \text{ mass loss} = \frac{4}{3} \times \frac{M_{bd} - M_{ad}}{M_{bd}} \times 100
\]  
(11)
3.1.2 Effect of silicone finishes on the burning behavior of “lofty” needlepunched polyester fabric

3.1.2.1 Effect of CT 205E silicone finishes on the burning behavior of PET

Using equation (11), the true % mass loss can be calculated to display the effect of a selected finish on a polyester fabric while controlling two parameters: heat treatment and amount of finish applied on the substrate, as shown in Figure 3.1. The CT205E technical instructions recommend that “the material should be properly cured to obtain the best result”. Thus, the influence of the curing step (heat treatment) was investigated as well. The % add-on value presented here is a calculated add-on based on solid contents of the finish. The difference between an untreated polyester fabric (0%) and a treated one is clearly shown, especially with add-on values of 1% and 2%. An untreated fabric has an average mass loss of 0.73% whereas 1% and 2% add-on have average mass losses of

![Figure 3.1: Comparison of % Mass loss of CT205E-treated PET fabric after diagonal flame test between heat treatment and no heat treatment vs. % add-on](image-url)
48% and 55% respectively, for heat treated samples. The effect seen at the 0.1% level is 
less drastic with average mass losses of 16% and 11% but the significant standard 
deviations denote a wide range of burning behavior for this add-on level. At this level 
some samples might burn completely while others may exhibit a behavior closer to an 
untreated sample. This can be explained by a lack of uniformity of the treatment, 
rendering the test output more sensitive to any variation in the basis weight of the fabric 
or in the flame length. For a given % add-on level, the heat treatment at 170°C for 10 
minutes has a slight effect on the % mass loss. At 1% add-on, the average mass loss 
increases from 48% to 60% between heat treated samples and the ones not heat treated, 
and from 55% to 63% at the 2% level add-on.

Figures 3.2 through 3.5 are photographs of polyester samples after a diagonal 
flame test showing the effect of the silicone-based treatment on the burning behavior. The 
visually most striking difference can be observed between an untreated PET sample 
(Figure 3.2) and the other treated PET samples. The untreated sample displays only a 
melting behavior with no trace of combustion whereas a treated sample exhibits combustion of the sample with black residue. Figure 3.3 shows the cases at a 0.1% level 
add-on where flaming occurred since some samples were visually closer to an untreated 
one for the reasons mentioned earlier.
Figure 3.2: Untreated PET fabric after diagonal flame test

Figure 3.3: Photographs of 0.1% add-on CT205E-treated PET fabric after diagonal flame test. (a) heat treated. (b) not heat treated
Figure 3.4: Photographs of 1% add-on CT205E-treated PET fabric after diagonal flame test. (a) heat treated. (b) not heat treated

Figure 3.5: Photographs of 2% add-on CT205E-treated PET fabric after diagonal flame test. (a) heat treated. (b) not heat treated
It is difficult if not impossible to identify the finish % add-on level based on the morphology of the sample after the diagonal flame test. The same goes between heat treatment and no heat treatment for a given % add-on. Based on the visual observations from the photographs in Figures 3.4 and 3.5 for instance, a mass loss close to 100% would be expected. The burnt and melted material accumulates along the edges of the frame, making the % mass loss less than expected. The other cause for deviation from actual mass loss is the lack of uniformity in the fabric basis weight.

**Flame-spread time (s) CT205E-treated PET fabric**

![Graph showing flame-spread time (s) for CT205E-treated PET fabric with heat treatment and no heat treatment vs. % add-on]

*Figure 3.6: Comparison of flame-spread time of CT205E-treated PET fabric after diagonal flame test between heat treatment and no heat treatment vs. % add-on*

The flame-spread time difference between the 1% and 2% add-on levels are shown in Figure 3.6. For 1% add-on the average flame-spread times are 13.6 s and 12.2 s between heat treated samples and not heat treated ones and 10.2 s and 7.1 s for 2%
add-on level. This length of time reveals how the flame reached the end of the fabric. A short flame-spread time would be expected to result into a lower % mass loss, however this is not the case here. Consequently, untreated polyester samples are not displayed here since they do not have a flame-spread time. In other cases, it should be noted that a null value in a flame-spread time does not necessarily imply that the fabric did not ignite, it just means that the flame did not spread far enough on the fabric to reach the cotton thread.

Table 3.1: Rates of flame-spread for CT205E-treated PET fabric

<table>
<thead>
<tr>
<th>% Add-on</th>
<th>Heat treatment (curing)</th>
<th>No heat treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1%</td>
<td>0.4 in.s⁻¹</td>
<td>0.4 in.s⁻¹</td>
</tr>
<tr>
<td>2%</td>
<td>0.5 in.s⁻¹</td>
<td>0.7 in.s⁻¹</td>
</tr>
</tbody>
</table>

The rate of flame-spread based on the 5” length and the average flame-spread time showed in Table 3.1 might not accurately reflect the entire burning process. A tall flame can reach the cotton thread thus triggering the stop watch while the lower regions of the sample might still be burning. At 0.1 % add-on, no flame-spread time was provided because of the large variations in the burning behavior.

3.1.2.2 Effect of curing time at 170°C on the burning behavior of treated nonwoven PET fabric

The second type of treatment was a crosslinking agent commonly said to procure a better encapsulation of the polyester fiber. The process requires heat treatment in order to cross link the silane coupler. The longer the sample is submitted to the heat treatment
process, the higher degree of cross linking is achieved [82]. It may be possible to calculate the amount of cross linking achieved by dissolving the polyester substrate and weighing the dry residue, since the cross-linked part would not be dissolved but only swell. Thus Figure 3.7 can be seen as showing the % mass loss obtained after flame testing at different levels of cross-linking. The average mass loss is slightly higher for the samples submitted to heat treatment with 69% compared to 55% for no heat treatment. With this type of finish, this difference may stem from the fibers being held in place and reducing the possibility of shrinking away.

The same conclusion can be reached when studying the flame-spread times on Figure 3.8. The flame-spread times are only slightly affected by the percentage of
cross-linking achieved, going from 8.4 s for no heat treatment up to 11.3 s for a 10 minute-treatment. The rates of flame-spread listed in Table 3.2 below are in the same order of the ones calculated for CT205E-treated samples.

**Table 3.2: Rate of flame-spread for SFC-treated PET fabric**

<table>
<thead>
<tr>
<th>Heat treatment time</th>
<th>Flame-spread rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 min</td>
<td>0.6 in.s⁻¹</td>
</tr>
<tr>
<td>5 min</td>
<td>0.5 in.s⁻¹</td>
</tr>
<tr>
<td>10 min</td>
<td>0.4 in.s⁻¹</td>
</tr>
</tbody>
</table>

**Flame-spread time SFC-treated PET fabric, 2% add-on**

![Flame-spread time SFC-treated PET fabric, 2% add-on](image)

*Figure 3.8: Flame-spread time of 2% add-on SFC-treated PET fabric after diagonal flame test vs. heat treatment time*

**3.1.2.3 Fourier Transform Infra-red (FTIR) spectroscopy on initial experiment**

When comparing the FTIR spectrum of a treated polyester fabric to a spectrum of an untreated one, we can isolate absorption peaks which allows them to be assigned to
specific groups. Figure 3.9 shows two peaks that can be used to detect the presence of silicone-based finishes on a polyester substrate. The prominent absorption peak emerging in the treated PET sample is located at 2962 cm\(^{-1}\), which is attributed to C-H\(_3\) antisymmetric stretching vibrations. The second one is located at 794 cm\(^{-1}\) and is attributed to Si-C stretching and CH\(_3\) antisymmetric rocking vibrations from the Si(CH\(_3\))\(_2\) group [83]. The other regions can not be used for detection of silicone-based finishes on a polyester substrate. Tables 3.3 and 3.4 lists the other regions where absorption peaks can be observed. For instance, the characteristic absorption peak for the PET substrate is located at 1712 cm\(^{-1}\) on both spectra of Figure 3.9, attributed to C==O stretching.
vibrations.

**Table 3.3: Possible FTIR absorption peaks in polyester sample [84]**

<table>
<thead>
<tr>
<th>Type of deformation</th>
<th>Characteristic absorption peak (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkanes: C—H stretching vibrations</td>
<td>3000-2850 cm(^{-1}) (m)</td>
</tr>
<tr>
<td>Alkanes: C—H deformations vibrations – (CH2)-</td>
<td>725-720 cm(^{-1}) (v)</td>
</tr>
<tr>
<td>Aromatic Compounds: C—H stretching vibrations</td>
<td>3080-3030 cm(^{-1}) (v-m)</td>
</tr>
<tr>
<td>Aromatic Compounds: C==H stretching vibrations</td>
<td>1625-1575 cm(^{-1}) (v)</td>
</tr>
<tr>
<td></td>
<td>1525 – 1475 cm(^{-1}) (v)</td>
</tr>
<tr>
<td></td>
<td>1590 – 1575 cm(^{-1}) (v)</td>
</tr>
<tr>
<td></td>
<td>1465 – 1440 cm(^{-1}) (v)</td>
</tr>
<tr>
<td>Aromatic Compounds: C—H out of plane deformations</td>
<td>860-800 cm(^{-1}) (s)</td>
</tr>
<tr>
<td>Aryl ester C==O stretching vibrations</td>
<td>1730 – 1715 cm(^{-1}) (s)</td>
</tr>
</tbody>
</table>

**Table 3.4: Possible FTIR absorption peaks in PDMS**

<table>
<thead>
<tr>
<th>Type of deformation</th>
<th>Characteristic absorption peak (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkanes C—H stretching vibrations</td>
<td>3000-2850 cm(^{-1}) (m)</td>
</tr>
<tr>
<td>Si—CH(_3)</td>
<td>1260 cm(^{-1}) and 1400 cm(^{-1})</td>
</tr>
<tr>
<td>Si—O bands</td>
<td>830 – 1110 cm(^{-1})</td>
</tr>
</tbody>
</table>
Figure 3.10 shows the effect of the % add-on of CT205E on the peaks intensities at 2962 cm\(^{-1}\) and 794 cm\(^{-1}\). Barely noticeable at 0.1% add-on, they appear more clearly at 1% add-on and their intensity increases at the 2% add-on level. FTIR spectroscopy could be used as a quantitative measurement tool as the % add-on seems to be proportional to the peak intensities. Figure 3.11 shows the effect of heat treatment on the absorption peaks location and intensities in the case of SFC treatment. No discernible difference can be observed between the two heat treated samples (5 min treatment or 10 min treatment). However, a slightly higher intensity at the 2962 cm\(^{-1}\) absorption peak can be seen on the spectra without heat treatment.
3.1.3 Effect of silicone finishes on the burning behavior of spunbond needled polyester fabric

In another preliminary study, the substrate was switched to a spunbond needled fabric to ensure a better thickness uniformity. The loftiness and lack of structural integrity of the needlepunched polyester substrate described in section 2.3.1.1 (see page 32) prevented the substrate from being completely soaked during treatment. In addition, this choice of substrate allows a better overview of the substrate treatment as well as an even distribution of the finish. The fabric was first analyzed through accelerated solvent extraction for any residual spin finishes that may be present on the fibers. The percent extractable based on weight recovery was computed using equation (12)

![Figure 3.11: FTIR spectra of SFC-treated fabric with different heat treatment times](image)
\[
\% \text{ Extractable by Weight recovery} = \frac{M_{\text{vial}'} - M_{\text{vial}}}{M_{\text{fabric}}} \times 100
\]  

(12)

Where

\( M_{\text{vial}'} \) = Mass of vial after extraction
\( M_{\text{vial}} \) = Mass of empty vial before extraction
\( M_{\text{fabric}} \) = Mass of fabric sample

Table 3.5: Results computed from ASE data

<table>
<thead>
<tr>
<th>Sample</th>
<th>% Extractable by Weight recovery</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.0020%</td>
</tr>
<tr>
<td>2</td>
<td>0.0037%</td>
</tr>
<tr>
<td>3</td>
<td>-0.0040%*</td>
</tr>
</tbody>
</table>

*: due to balance error

Table 3.5 shows that the spunbond fabric did not contain any finishes, since the low values obtained stem from the balance variations or changes in temperature. Thus we can confirm that control samples referred to as untreated polyester are in fact finish free.

3.1.3.1 Effect of PDMS fluid viscosity on burning behavior of PET in diagonal flame test

Figure 3.12 shows the effect of conventional silicone fluids PDMS A and PDMS B on the burning behavior of a polyester spunbond nonwoven fabric. The substrate was treated with PDMS A or PDMS B dissolved in hexane which then evaporated, as described in section 2.3.2.2 (see page 37). Table 3.6 lists the differences between the two PDMS A and PDMS B products.
Effect of viscosity on % mass loss of treated PET fabric

![Figure 3.12: % mass loss of different viscosity PDMS-treated PET fabric after diagonal flame test vs. % owf](image)

Table 3.6: PDMS A and PDMS B products properties

<table>
<thead>
<tr>
<th>PDMS</th>
<th>Viscosity</th>
<th>Molecular weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1000 cSt</td>
<td>28,000 g.mol⁻¹</td>
</tr>
<tr>
<td>B</td>
<td>350 cSt</td>
<td>13,650 g.mol⁻¹</td>
</tr>
</tbody>
</table>

Once again, the average mass loss of a treated sample is considerable when compared to an untreated one which has an average of 0.2%. PDMS A shows average mass losses between 25% and 10% whereas PDMS B average mass losses stay between 12% and 16%. The small sample size make them more sensitive to variations in fabric basis weight, which affects the computed % mass loss. Yet, the effect of the amount of finish present on the fibers does not seem to have any effect on the average mass loss,
pointing to the fact that the finish does not act as an additional source of fuel. Based on the % owf levels, %add-on should be between 4% and 25%. No flame-spread time is provided here since only a few samples burned far enough to reach the cotton thread. Their flame-spread time was 30 s on average.

% Mass loss SR-treated PET fabric

![Figure 3.13: % Mass loss of SR-treated fabric after diagonal flame test vs. % owf](image)

Figure 3.13 shows the difference between a silicone-based finish and a polyester-based one. The SR finish (non silicone-based softener) does have a small effect on the % mass loss compared to an untreated sample. This behavior is expected since any modifications or treatments done to the sample will modify its burning behavior. At 62.5% owf, the average mass loss for SR-treated sample is only 3% with a low value of 0.4% at 6.25% owf. When compared to PDMS B for instance, its influence on the % mass loss is closer to the behavior of an untreated sample. Silicone-based finishes will
result in a flaming sample whereas SR-treated ones may or may not reach the flaming stage. In the cases where a flame was produced, the sample would quickly extinguish by dripping, resulting in the low mass losses computed. However a direct comparison is difficult since the % owf does not accurately reflect the actual amount of finish present on the fabric.
3.1.3.2 FTIR Spectroscopy

Absorbance ratio for characteristic peaks in PDMS A-treated PET fabric

\[ \text{Absorbance ratio (\%)} \]

![Figure 3.14: Absorbance ratio for characteristic peaks in PDMS-A treated PET fabric vs. \% owf](image)

By using the characteristic absorption peaks described in section 3.1.2.3 (see page 58) and the characteristic absorption peak for PET (1712 cm\(^{-1}\)), the absorbance ratio can be plotted against the \% owf applied to the PET fabric. Figures 3.14 and 3.15 display the proportionality between the amount of finish present on the fabric and the absorbance ratios for 2962 cm\(^{-1}\) and 791 cm\(^{-1}\) gathered from the FTIR spectra of PDMS A and PDMS B treated PET fabric samples.

The large errors make this process uncertain in the proper assessment of the amount of finish present from one \% owf relative to another. Only with large differences in the \% owf treatment, between 6.25\% and 62.5\% for instance, is it possible to better quantify the \% add-on obtained.
3.2 Central investigation into the effect of silicone finishes on the burning behavior of PET

The burning behavior was investigated through the vertical flame test in order to overcome the shortcomings observed in the preliminary study. The initial examination employed the diagonal flame test (45°) to assess the burning behavior of polyester. In addition, the treatment process resulted in a more accurate estimation of the amount of finish present on the spunbond polyester fabric. Figure 3.16 shows the proportionality observed between the % owf and the actual % add-on obtained on the fabric for the different finishes used in this study. As explained in section 2.2 (see page 31), % owf refers to the finish product to be applied whereas % add-on is the amount of finish present on the substrate after drying.
Figure 3.16: % add-on obtained for different types of finishes on PET fabric vs. % owf

Figure 3.17: % add-on obtained for different types of finishes on PET film
Figure 3.17 shows the % add-on obtained through the film coating technique described in section 2.4.2.2 (see page 40). Large differences in the amount of finish being trapped between the two layers of film can be noticed, due to the differences in viscosities as well as type of dispersion.
3.2.1 Observations of samples photographs after submission to vertical flame test

3.2.1.1 Photographs of untreated polyester samples after vertical flame test

The untreated polyester fabric seen in Figure 3.18 (a) only shows melting behavior when subjected to a flame in a vertical flame chamber. The fabric shrinks away when in direct contact with the flame and the higher portion of the sample melts too due to the heat generated by the flame. The final shape of the sample resembles the shape of

Figure 3.18: Photographs of untreated polyester substrates after vertical flame test
(a) Spunbond fabric. (b) Film.
the flame, without any char on the sides. However, the molten fabric edges may appear brown and yellow if it is heated to a temperature high enough above its 256°C melting point, between 280°C and 325°C [85]. In addition, ignition may occur in the form of a small flame but it will extinguish rapidly and not propagate. This comes from the lack of uniformity in the fabric thickness and fabric density. The top part of the shape narrows as only the heat transfer by convection occurs as described in the sample schematic in Figure 3.19 above. The untreated polyester film shown in Figure 3.18 (b) exhibits the

Figure 3.19: Schematic of heat transfers from a flame to an untreated PET fabric.
same behavior to a larger extent, the sample mass being half the one of the spunbond fabric. In both cases, the remaining substrate display solid, glassy edges where the polymer solidified after removal of the flame.

### 3.2.1.2 Photographs of silicone-treated spunbond polyester fabric samples after vertical flame test

Silicone-treated polyester fabric samples were photographed after being subjected to a vertical flame test with a 12 s ignition. For each treatment showed, one photograph was selected out of five samples to demonstrate the effect of the silicone treatment on the burning behavior of the polyester substrate.

Figure 3.20 are photographs displaying PDMS A-treated samples with 0.1% owf, 5% owf and 50% owf respectively after being submitted to a vertical flame test. Major differences can be seen from an untreated polyester sample. For instance, the treated polyester does not exhibit the flame-shaped section at the top of the missing area as in an untreated sample. Upon ignition, flames progress rapidly, leading to large yellow flames which progress across the fabric but stop before reaching the end of the sample. The lower vertical edges of the fabric are charred and droplet shaped charred residues accumulated along the edges of the frame. The top part of the missing area exhibits some melted areas in the shape of an arch due to the heat transferred by convection from flames propagating along the sample. Even at a low level of 0.1% owf, a difference can be seen between a control sample (untreated) and a treated one. The flame did not propagate as far as the higher % owf, leaving more glassy edges toward the top part of the sample.
Based on the appearance of the treated samples, the amount of finish is irrelevant. Indeed, the samples burn the same way once treated. If the finish was an added source of fuel, one would expect to be able to differentiate samples based on the remaining fabric after a flame test. Consequently, the amount of finish present on the fabric does not act as a fuel source.
A similar type of burning behavior and subsequent patterns can be seen with PDMS B-treated samples in Figure 3.21. Similarly to PDMS A-treated samples, the lack of significant visual difference between the two extreme level of 0.1% owf (3.21(a)) and 50% owf (3.21(b)) would suggest that the finish added to the fabric does not act as a fuel source.

Figure 3.21: Photographs of PDMS B-treated polyester fabric after vertical flame test. (a) 0.1% owf. (b) 5% owf. (c) 50% owf.
CT205E-treated polyester fabric samples exhibit a comparable burning behavior over the same range of % owf levels as well, as shown in Figure 3.22. Similarly to PDMS A and PDMS B treatments, the residues located along the edges of the sample holder are constituted of very friable black ashes. Some melt dripping can be seen extending from the bottom part of the remaining fabric as well as melted arches. Once again, remaining samples are visually indistinguishable one % owf from another, the only difference being between an untreated sample and untreated ones.
In the case of AF2340-treated polyester fabric samples shown in Figure 3.23, the lowest % owf level shows a more prominent convection induced peak at the top of the missing portion of the fabric. However, ignition and subsequent flame propagation occurred in all cases. Additionally, with noticeable friable ashy residues were located alongside the edges of the sample holder, indicating prolonged combustion in the cases of higher % owf (Figures 3.23 (b) and 3.23 (c)). At 0.1% owf, (Figure 3.23 (a)) the residue on the edge indicate a predominant melting behavior with a shorter combustion time than...
the other samples.

Figure 3.24: Photographs of Powersoft-treated polyester fabric after vertical flame test.
(a) 0.1% owf. (b) 5% owf. (c) 50% owf.

The Powersoft-treated samples displayed in Figure 3.24 become visually similar to an untreated sample as the % owf reaches 0.1%. At the lowest level of % owf shown in Figure 3.24 (a) the convection induced shape and smoother edges become discernible, indicating a melting type behavior. With higher levels of finish (Figures 3.24 (b) and 3.24 (c), extended periods of combustion effects were observed on the remaining sample.
having friable black residues.

Figure 3.25: Photographs of Wetsoft-treated polyester fabric after vertical flame test. (a) 0.1% owf. (b) 5% owf. (c) 50% owf.

In the case of the Wetsoft-treated polyester fabric samples shown in Figure 3.25, a similar burning behavior can be observed, with a slightly more pronounced tendency for melt dripping, a seen in Figures 3.25 (b) and 3.25 (c) for instance. However, this tendency does not significantly modify the burning behavior or the shape of what remains of the fabric after combustion. In all cases, friable black residues were visible alongside the edges of the sample holder.
Finally, SE26-treated polyester fabric samples, shown in Figure 3.26 exhibit a comparable behavior to the other finishes described previously. Friable residues alongside the edges of the sample holder can be seen for higher % owf (Figures 3.26 (b) and 3.26 (c)). In addition, a convection induced peak starts appearing at the 0.1% owf level (Figure 3.26 (a)). with a predominantly melting behavior near the bottom edges.

Despite the differences between the % owf levels of silicone finishes, the burning
behaviors of the treated spunbond polyester substrate remain similar. Regardless of the chemistry, a small amount of these materials will affect the burning behavior of the treated substrate.

3.2.1.3 Photographs of silicone-treated polyester film samples after vertical flame test

Polyester film samples treated using the technique described earlier in section 2.4.2.2 (see page 40) were submitted to a vertical flame test and photographed to investigate the effect of silicone finishes on a thin surface of the order of a fiber dimension.

Figures 3.27, 3.28 and 3.29 show the resulting samples of silicone-treated polyester films after being submitted to a vertical flame test. Compared to each other, the treated film samples display different burning behaviors since a different % add-on is obtained through the coating technique, depending upon the type of finish as seen in Figure 3.17 earlier. The silicone fluids PDMS A and PDMS B shown in Figures 3.27 (a) and 3.27 (b) do not seem to greatly affect the melting behavior of the polyester film, as the visual result is very close to an untreated sample (Figure 3.18 (b)).
As shown in Figure 3.27 (c), the finish CT205E has very noticeable effect on the polyester film when subjected to a flame. Rapid ignition occurs, followed by flaming combustion, leaving black and friable residues along the edges of the sample holder.

Figure 3.27: Photographs of silicone-treated polyester films after vertical flame test. (a) PDMS A. (b) PDMS B (c) CT205E
The same effect can be witnessed in Figure 3.28 with films treated with finishes Powersoft and Wetsoft. Ignition quickly occurs once the sample is in contact with a flame, followed by rapid flame spreading. The melting by convection process is hardly noticeable in this case.

Finally, the films treated with AF2340 and SE26 finishes as shown in Figure 3.29 behave the same way as previously described. Friable residues accumulates along the
sample holder edges and the arched shape seen at the top of the missing portion stem from heat generated by large flames propagating near the edges.

### 3.2.1.4 Photographs after vertical flame test of polyester samples treated with non-silicone-based finishes

In the case where the polyester fabric substrate was treated with a non-silicone based softening agent, the melting behavior dominates and compares well to an untreated sample as seen in Figure 3.18. As such, the flame does not spread vertically and the
sample quickly extinguishes as shown in Figure 3.30. In the case of a low % owf as seen in Figure 3.30 (a), the shape of the remaining sample displays a tall convection induced peak and compares well to the final shape of an untreated sample. With a higher amount of finish SR (Figures 3.30 (b) and 3.30 (c)), this convection peak appears to be slightly broadening. In conclusion, SR-treated polyester fabric samples exhibit a behavior very similar to untreated samples when being subjected to a vertical flame test.

Figure 3.30: Photographs of SR-treated polyester fabric after vertical flame test. (a) 0.1% owf. (b) 5% owf. (c) 50% owf.
In some formulations, surfactants are used to help spread finishes. In this context, they may be considered as a non-polymeric source of carbon fuel. When the polyester substrate is treated with Triton surfactant, this apparently additional source of fuel does not impart the melting behavior of polyester when subjected to a flame as shown in Figure 3.31. Even if ignition occurs, the fabric quickly extinguishes, thus ending up with smooth black edges. A similar convection induced peak can be seen for all % owf levels.

Figure 3.31: Photographs of Triton-treated polyester fabric after vertical flame test. (a) 10% owf. (b) 20% owf. (c) 50% owf.
This peak is broadened with a higher finish content (Figure 3.31 (c)). Once again, the final shape of the remaining fabric is comparable to the one of an untreated sample. Even at 50% owf (18% add-on), the treated sample still behaves differently than treated with a polymeric finish.

Pluronic surfactant appears to have a more significant effect on the substrate after ignition. Nonetheless, the remaining samples still exhibit similar trends to Triton-treated
sample and a clear melting behavior as seen in Figure 3.32. Melt dripping as well as a convection induced peak are present in all cases, with solid glassy edges indicating a combustion too short to induce friable residues.

Sodium Silicate (Na$_2$SiO$_3$) was applied as a fabric treatment to investigate the influence of the Silicon element Si in a non polymeric form. The low level was chosen to be on par with the threshold effect of polymeric silicon. In this trial, shown in Figure 3.33, despite the ignition of the sample for a short duration, the convection induced peak is still very much present and the final shape very close to an untreated sample.
Figure 3.33: Photograph of Sodium silicate-treated PET fabric after flame test
Figure 3.34: Photograph of SR-treated PET film after vertical flame test
The SR treated polyester film shown in Figure 3.34 exhibited a rapid ignition followed by some flaming combustion but the melting phenomenon is still present.

3.2.2 Mass loss of polyester samples after vertical flame test

3.2.2.1 Corrected mass loss calculations used for vertical flame test

The same correction as seen in equation (11) in section 3.1.1 (see page 50) needs to be used here since Figure 2.10 (see page 42) shows that only 2” out of 3” of the sample width could be consumed by the flame, assuming no flame spread inside the metal frame “sandwich”. Making analogous assumptions used for equation (8) (see page 50), we have

\[ \% \text{ corrected mass loss} = \frac{M_{bv} - M_{av}'}{M_{bv}'} \times 100 \] (13)

with

\[ M_{bv}' = M_{bv} - \frac{1}{3} \times M_{bv} \] (14)

\[ M_{av}' = M_{av} - \frac{1}{3} \times M_{bv} \] (15)

Where

\( M_{bv} \)= Mass of sample before vertical flame test
\( M_{av} \)= Mass of sample after vertical flame test

Thus the true mass loss can be computed using equation (16)

\[ \% \text{ mass loss} = \frac{3}{2} \times \frac{M_{bv} - M_{av}}{M_{bv}} \times 100 \] (16)
3.2.2.2 % Mass loss of silicone-treated spunbond polyester fabric samples after vertical flame test

The % mass loss values were calculated using equation (16) from the previous section. Surprisingly, the % mass loss can appear low when looking at a sample after being submitted to a vertical flame test. For example, for an untreated sample, the shrinking behavior leads to a substantial area loss with almost no mass loss. Indeed, for some samples the area loss would suggest a 50% mass loss. However, this phenomenon is not unheard of, with scale models cars where part of the mass loss was due to the loss of unburnt volatiles [86]. This discrepancy between photographic and gravimetric data can be explained by the fact that during combustion part of the polyester forms droplets which burn at the surface, forming a protective char layer thus preventing the droplet from being completely burned by the flame [87].

For the lowest % owf level (0.1%), % add-on values can be greater than 0.1%, since the samples moisture content is between 0.2% and 0.3%. For heavier % owf levels, this small discrepancy is not detectable.
The effect of PDMS A on the % mass loss of the polyester fabric can be seen in Figure 3.35 side by side with the actual amount of finish present on the fabric, expressed as % add-on. In the situation where we consider the finish as a supplementary fuel source, the expected consequence would be an increase in the % mass loss when increasing the % add-on. However, this is not the case here as the mass loss is rather consistent, staying within 10% to 18% over a wide range of % add-ons with a slight decrease toward the end of the spectrum. Even at very low level of 0.10% average add-on, the effect of the silicone fluid has a dramatic effect on the resulting % mass loss compared to an untreated sample having an average mass loss of 0.42%.

The same behavior can be seen with the % mass loss of PDMS B-treated
polyester fabric samples in Figure 3.36, where the average mass loss fluctuates between 8% and 20% over % add-on from 0.14% to 21%. The same tendency of a decreasing % mass loss as the amount of finish increases may be explained by the silicone fluid forming a protective layer around the polyester fiber, thus hindering the flame progression.

The effect of CT205E treatment on the % mass loss shown in Figure 3.37 is also clear at low levels at 0.19% add-on with an average mass loss of 16%. As the amount of finish on the fabric increases up to 22% add-on, the average mass loss remains between 14% and 20%. It can be deduced that this finish does not act as a source of fuel but rather as a trigger of the fabric ignition process, even at very low levels.
Figure 3.37: % Mass loss of CT205E-treated PET fabric after vertical flame test vs. % owf

Figure 3.38: % Mass loss of Powersoft-treated PET fabric after vertical flame test vs. % owf
The Powersoft-treated polyester fabric example shown in Figure 3.38 seems to be more sensitive regarding the % add-on as compared to previous finishes since the average mass loss is only 8% at 0.2% add-on. Nevertheless, it is still an abrupt departure from the 0.42% average mass loss of an untreated sample, with almost twenty times the % mass loss of an untreated sample. As the % add-on reaches 12%, the average mass loss stays within 16% and 19%, very similar to the other finishes described previously. Once again, this behavior goes against the supplementary fuel hypothesis.

% Mass loss Wetsoft-treated PET fabric

Figure 3.39: % Mass loss of Wetsoft-treated PET fabric after vertical flame test vs. % owf

Wetsoft-treated samples shown in Figure 3.39 exhibit the same ranges of consistent mass loss, staying between 13% and 18% of average mass loss with add-on levels going from 0.19% up to 28%. The presence of the finish on the fabric triggers an
ignition and subsequent flame spreading, phenomena then independent from the quantity of finish.

The effect of finish AF2340 shown in Figure 3.40 displays a behavior very similar to Powersoft as the lower end of the spectrum results in an average mass loss of 10% with 0.15% add-on. The rest of the samples average mass loss fluctuates between 17% and 22%, for add-on between 0.5% and 18%. This behavior is in agreement with what has been observed so far, as the % mass loss does not vary greatly, regardless of the amount of finish present on the fabric.

![% Mass loss AF2340-treated PET fabric](image)

*Figure 3.40: % Mass loss of AF2340-treated PET fabric after vertical flame test vs. % owf*

Finally, the behavior of SE26-treated polyester samples in a vertical flame test shown in Figure 3.41 are less influenced by a low level of % add-on, resulting in an 8%
average mass loss with 0.12% add-on. As the % add-on increases from 0.26% to 11%, the average mass loss stays within 17% and 21% which corresponds to what has been observed with finishes previously described.

3.2.2.3 % Mass loss after vertical flame test of spunbond polyester fabric samples treated with non-silicone based finishes

In the case of SR-treated PET fabric shown in Figure 3.42, average mass losses stay well below 10%. At the lowest % add-on of 0.12%, the average mass loss is only about 2%, whereas it fluctuates between 4% and 6% with higher amounts of finish on the fabric. Adding this finish modifies the response of polyester to a flame, but no major flame spreading occurs as the melting behavior dominates the reaction.
**% Mass loss SR-treated PET fabric**

![Diagram showing % Mass loss for SR-treated PET fabric](image1)

*Figure 3.42: % Mass loss of SR-treated PET fabric after vertical flame test vs. % owf*

**% Mass loss Triton-treated PET fabric**

![Diagram showing % Mass loss for Triton-treated PET fabric](image2)

*Figure 3.44: % Mass loss of Triton-treated PET fabric after vertical flame test vs. % owf*
The same conclusion can be reached when studying Figure 3.44 above, as the effect of Triton on the mass loss is well below what has been observed with silicone-based finishes. As the % add-on goes from 7% up to 16%, the average mass loss remains between 2% and 5%.

% Mass loss Pluronic-treated PET fabric

![Graph of Mass loss Pluronic-treated PET fabric](image)

*Figure 3.43: % Mass loss of Pluronic-treated PET fabric after vertical flame test vs. % owf*

As suggested by the photographic evidence earlier, Pluronic-treated PET fabric (Figure 3.43) shows slightly higher mass losses than Triton-treated fabric but its average mass loss does not go above 7%. Similar to the SR finish, the surfactants modify the flame response of polyester but not enough to generate the spreading of the flame after ignition.
% Mass loss Sodium Silicate-treated PET fabric

![Graph showing % Mass loss of sodium silicate-treated PET fabric vs. % owf](image)

Figure 3.45: % Mass loss of sodium silicate-treated PET fabric after vertical flame test vs. % owf

When compared to the silicone fluids PDMS A and PDMS B, the effect of sodium-silicate treatment on the mass loss of the polyester fabric, shown in 3.45 below, appears trivial with an average of 3% at an 0.2% add-on. The mere presence of silicon (Si) at this level does not trigger a flaming response like the ones seen in the cases of silicone fluids at similar add-ons.

3.2.3 Area loss of polyester samples after vertical flame test

3.2.3.1 % Area loss of silicone-treated spunbond polyester fabric samples after vertical flame test

As indicated by the photographic evidence presented in section 3.2.1.2 (see page 73), the expected area loss from the original sample would be near 50% for most of the samples. PDMS A-treated PET fabric samples maintain an average area loss between
45% and 49%, as presented in Figure 3.46. Very little of this loss is due to convection shrinkage, as opposed to an untreated sample having a 16% area loss average, none of it due to actual burning.

Similarly, the % area missing in PDMS B-treated samples follow the same trend, as presented in Figure 3.47, with averages ranging between 40% and 51%.
Figure 3.47: % Area loss of PDMS B-treated PET fabric after vertical flame test vs. % owf

Figure 3.48: % Area loss of CT205E-treated PET fabric after vertical flame test vs. % owf
Not surprisingly, CT205E-treated fabric samples display averages within the same narrow ranges as shown in Figure 3.48. Despite the large difference in % add-on levels, the average area loss stays between 45% and 50%.

% Area loss Powersoft-treated PET fabric

![% Area loss Powersoft-treated PET fabric after vertical flame test vs. % owf](image)

*Figure 3.49: % Area loss of Powersoft-treated PET fabric after vertical flame test vs. % owf*

As stated earlier, the effects observed at the lowest % add-on of Powersoft being less potent, this behavior is observed in the % area loss as well, as shown in Figure 3.49 below. At 0.2% add-on, the average area loss is only 36% whereas for the rest of the % add-on levels, it ranges between 43% and 50%.

The Wetsoft-treated fabric is also within the same range, fluctuating between 41% and 49% average % area loss, as seen in Figure 3.50.
% Area loss Wetsoft-treated PET fabric

Figure 3.50: % Area loss of Wetsoft-treated PET fabric after vertical flame test vs. % owf

% Area loss AF2340-treated PET fabric

Figure 3.51: % Area loss of AF2340-treated PET fabric after vertical flame test vs. % owf
AF2340-treated polyester samples, presented in Figure 3.51, display an average area loss between 40% and 56%, once again in the same range as the other finishes previously described.

**% Area loss SE26-treated PET fabric**

![Graph: % Area loss SE26-treated PET fabric after vertical flame test vs. % owf](image)

*Figure 3.52: % Area loss of SE26-treated PET fabric after vertical flame test vs. % owf*

Finally, SE26-treated polyester samples, presented in Figure 3.52 behave in a similar fashion with an average area loss between 40% and 54%.

3.2.3.2 % Area loss after vertical flame test of spunbond polyester fabric samples treated with non-silicone based finishes

From the photographs displayed in section 3.2.1.4 (see page 84), the average area loss exhibited with SR-treated polyester samples shown in Figure 3.53, is under 40%.
Figure 3.53: % Area loss of SR-treated PET fabric after vertical flame test vs. % owf

Figure 3.54: % Area loss of Triton-treated PET fabric after vertical flame test vs. % owf
The effect of Triton on the % area loss of polyester fabric samples seen in Figure 3.54 remains limited, as the average area missing is within 27% and 31%.

As suggested by the Figures 3.31 and 3.32 photographs, Pluronic-treated polyester fabric samples are more damaged by a flame than Triton-treated samples. The % area loss displayed in Figure 3.55 is slightly higher than for Triton, ranging between 35% and 44%.

% Area loss Pluronic-treated PET fabric

![Graph showing % Area loss Pluronic-treated PET fabric](image)

*Figure 3.55: % Area loss of Pluronic-treated PET fabric after vertical flame test vs. % owf*

Finally, as sodium-silicate-treated PET fabric mainly displays a melting behavior, the 33% average area loss remains below the ones showed for PDMS A and PDMS B, as seen in Figure 3.56.
3.2.4 After-flame times of polyester samples measured during vertical flame test

It should be noted that computing a rate of flame-spread based on the sample length consumed during the vertical flame test and the after-flame time would not accurately reflect the burning process since the lower regions of the sample might still be burning while the flame has ceased to spread. In addition, as described earlier, the flame may not have actually reached the top part, since the area loss can be due to a convection phenomenon and not due to combustion. Finally, it should be reminded that a null value does not necessarily mean that there was no flame but that the flaming stopped within the 12 seconds during which the burner flame was applied to the sample. In addition, in cases where rapid ignition occurs, the total combustion time is in fact the after-flame time added to the 12 second impingement time.

Figure 3.56: % Area loss of Sodium Silicate-treated PET fabric after vertical flame test vs. % owf

% Area loss Sodium Silicate-treated PET fabric

Figure 3.56: % Area loss of Sodium Silicate-treated PET fabric after vertical flame test vs. % owf

3.2.4 After-flame times of polyester samples measured during vertical flame test

It should be noted that computing a rate of flame-spread based on the sample length consumed during the vertical flame test and the after-flame time would not accurately reflect the burning process since the lower regions of the sample might still be burning while the flame has ceased to spread. In addition, as described earlier, the flame may not have actually reached the top part, since the area loss can be due to a convection phenomenon and not due to combustion. Finally, it should be reminded that a null value does not necessarily mean that there was no flame but that the flaming stopped within the 12 seconds during which the burner flame was applied to the sample. In addition, in cases where rapid ignition occurs, the total combustion time is in fact the after-flame time added to the 12 second impingement time.
3.2.4.1 After-flame times of silicone-treated spunbond polyester fabric samples measured during vertical flame test

After-flame time (s) PDMS A-treated PET fabric

Figure 3.57: After-flame times of PDMS A-treated PET fabric after vertical flame test vs. % owf

PDMS A-treated polyester fabric samples (Figure 3.57) display after-flame times in the range of 22 to 32 seconds, which translate to a combustion duration between 34 and 44 seconds. This length of time may appear long considering the % mass loss. This phenomenon does correlate with what has been witnessed earlier concerning the flaming droplets accumulating along the edges of the sample holder.

The same after-flame time range can be observed in the case of PDMS B-treated polyester samples (Figure 3.58), as the same phenomenon occurs during the vertical flame test, with after-flame times between 21 and 33 seconds.
After-flame time (s) PDMS B-treated PET fabric

![Graph showing after-flame times for PDMS B-treated PET fabric after vertical flame test versus % owf.]

Figure 3.58: After-flame times of PDMS B-treated PET fabric after vertical flame test vs. % owf

After-flame time (s) CT205E-treated PET fabric

![Graph showing after-flame times for CT205E-treated PET fabric after vertical flame test versus % owf.]

Figure 3.59: After-flame times of CT205E-treated PET fabric after vertical flame test vs. % owf

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Polyester samples treated with the CT205E finish (shown in Figure 3.59) display a narrower range of average after-flame time for add-ons greater than 0.19%, fluctuating between 24 and 26 seconds. At 0.19% add-on, the low average of 16 seconds also points to some melting behavior.

**After-flame time (s) Powersoft-treated PET fabric**

![Figure 3.60: After-flame times of Powersoft-treated PET fabric after vertical flame test vs. % owf](image)

In agreement with the % mass loss and the % area loss described earlier, the lack of influence of Powersoft on the polyester fabric burning behavior at the lowest % add-on can be seen in Figure 3.60. At this level, the average after-flame time is close to 8 seconds whereas it ranges between 20 and 28 seconds for higher amounts of finish.
The Wetsoft-treated PET fabric shown in Figure 3.61 above displays a lower range of average after-flame times than the ones previously seen with silicone fluids PDMS A and PDMS B for instance. The average after-flame times are between 15 and 24 seconds, indicating a very rapid combustion.

The effect of AF2340 on the after-flame time shown in Figure 3.62, displays the same range of average after-flame time for % add-on levels greater than 0.15%. Despite large variations, the average remains between 20 and 27 seconds. Once again, at 0.15%, the behavior becomes more erratic with a lower average after-flame time of 14 seconds.
After-flame time (s) AF2340-treated PET fabric

![Graph showing after-flame times of AF2340-treated PET fabric after vertical flame test vs. % owf]

Figure 3.62: After-flame times of AF2340-treated PET fabric after vertical flame test vs. % owf

After-flame time (s) SE26-treated PET fabric

![Graph showing after-flame times of SE26-treated PET fabric after vertical flame test vs. % owf]

Figure 3.63: After-flame times of SE26-treated PET fabric after vertical flame test vs. % owf
Finally, SE26-treated polyester samples shown in Figure 3.63 display a similar behavior with a range of average after-flame times between 21 and 26 seconds for % add-on levels greater than 0.12%. At 0.12%, the average is much lower, with a 13s after-flame time and showing a less predictable behavior.

### 3.2.4.2 After-flame times of spunbond polyester fabric samples treated with non-silicone based finishes measured during vertical flame test

**After-flame time (s) SR-treated PET fabric**

![Graph showing after-flame times of SR-treated PET fabric vs. % owf](image)

*Figure 3.64: After-flame times of SR-treated PET fabric after vertical flame test vs. % owf*

Substantial deviations observed in the after-flame times of SR-treated PET fabric from Figure 3.64 point to a predominantly melting behavior. Once again the data obtained are quite different from what has been observed with silicone based finishes.

Similarly, Triton-treated polyester fabric after-flame times shown in Figure 3.65 below correlate well with the previous data. As previously stated, large deviations stem
from the zero values obtained in the case where there is no ignition or if the sample flame ceases before the removal of the burner flame.

**After-flame time (s) Triton-treated PET fabric**

![Graph showing after-flame times of Triton-treated PET fabric](image)

*Figure 3.65: After-flame times of Triton-treated PET fabric after vertical flame test vs. % owf*

The Pluronic-treated polyester fabric data shown in Figure 3.66 displays the same shorter after-flame time averages with large deviations, also pointing to predominantly melting behavior.

Finally, the effect of sodium silicate on the after-flame times of polyester fabric seen in Figure 3.67 indicates a lack of significant effect on the behavior of the sample when subjected to a flame.
After-flame time (s) Sodium Silicate-treated PET fabric

Figure 3.67: After-flame times of Sodium Silicate-treated PET fabric after vertical flame test vs. % owf

After-flame time (s) Pluronic-treated PET fabric

Figure 3.66: After-flame times of Pluronic-treated PET fabric after vertical flame test vs. % owf

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3.2.5 % Mass loss, % area missing and after-flame time of polyester film samples after vertical flame test

% Mass loss PET film substrate vs. type of finish

![Bar chart showing % Mass loss PET film substrate vs. type of finish]

Figure 3.68: % Mass loss of treated PET film substrates after vertical flame test vs. type of finish

In the case of the treated film substrate data shown in Figure 3.68, the large differences in the % add-on level make it difficult to determine a trend in the average mass loss. Similarly, the % area loss shown in Figure 3.69 presents large deviations.

Finally, the after-flame times for treated polyester films shown in Figure 3.70 display large deviations due to behavior switching from sustained combustion to short flame spreading and mostly melting behavior.
% Area loss PET film substrate vs. type of finish

![Area loss graph](image)

*Figure 3.69: % Area loss of treated PET film substrates after vertical flame test vs. type of finish*

After-flame time (s) PET film substrate vs. type of finish

![After-flame time graph](image)

*Figure 3.70: After-flame times of treated PET film substrates after vertical flame test vs. type of finish*
3.2.6 Overall behavior of spunbond polyester nonwoven substrate in vertical flame test

Once treated with a silicone-based finish, the polyester spunbond fabric exhibits behaviors different than an untreated fabric in a vertical flame test. A wide array of silicone finishes with different functionalities, different viscosities and different end uses results in similar burning behaviors. After flame impingement, the samples rapidly ignite, displaying large yellow flames. These flames progress vertically to roughly halfway of the total possible testing area when the combustion ceases as the sample self extinguishes. At that point, the heat generated by the flames is not enough to reach the pyrolysis temperature of the next ignition zone, as displayed in Figure 3.71 below, breaking the combustion cycle. The heat generated by the combustion phenomenon at this point only melts some portions of the remaining sample by convection.

Figure 3.71: Schematic of vertical flame spread (adapted from Hull et al. [37] Figure 5)
In this vertical setup with bottom ignition, the difference between a silicone-treated sample and an untreated one is apparent. However, once the ignition process is initiated, it becomes impossible to differentiate the type of silicone finish used and the amount applied on the substrate. Consequently, the burning behavior does not depend upon the type of functionality nor the end groups of the silicone finish. Whether it is a simple PDMS fluid or an amino functional softener, the sample will ignite and present similar burning residues.

The silicone finish appears to hinder the inherent tendency of the polyester substrate to contract and shrink away from the heat source. Since polydimethylsiloxanes form a flexible surface film over the fibers, even at very low % add-on, the fabric becomes less able to move freely when a source of heat is applied. It has been noted that during some heating treatments, such as hot ironing, the polysiloxane film can not be melted, nor can it flow together [20]. This behavior may be sufficient enough to prevent the polyester from shrinking away fast enough, thus leaving the substrate in the vicinity of the heat source long enough to trigger the ignition process, leading into a chain reaction.

This theoretical behavior is only valid under these circumstances. Differences in ignition behavior might not be so noticeable using a different substrate shape. For instance, under vertical testing, an increase in sample density and a configuration where the contraction of the sample would be impeded may result in similar remaining burnt residues.
3.3 Thermogravimetric analysis

The significance of thermoanalytical measurements in the assessment of polymer flammability has been previously discussed. It was concluded that thermoanalytical measurements could not accurately represent the complex process of polymer combustion [88]. The overall thermal stability might not be a good indicator of the material flammability. Typical rates in thermal analysis are $10^\circ \text{C. min}^{-1}$ to $25^\circ \text{C. min}^{-1}$ whereas in flame test the temperature will reach at least $900^\circ \text{C}$ in a matter of seconds. The amount of heat exchanged will be much greater in an actual fire, with surface heating rates near $10^7 \text{ J.s}^{-1}.\text{m}^{-2}$. Consequently, the data obtained here must be treated carefully. It should be kept in mind that these measurements do not necessarily reflect the degradation behavior observed during the vertical flame test.

3.3.1 Thermograms of spunbond polyester samples

3.3.1.1 Thermograms of silicone-treated spunbond polyester samples

The thermogravimetric analysis (TGA) and differential thermogravimetric analysis (DTGA) curves shown in Figures 3.72 to 3.85 display the thermal degradation of silicone-treated polyester fibers in air. Most prior TGA experiments of polyester fibers, whether silicone treated or untreated, stop near $600^\circ \text{C}$, showing large amounts of residues at the end of the thermal degradation process. When the temperature is increased to $1000^\circ \text{C}$, a second transition in the degradation process can be seen. This second step does not occur in a inert atmosphere such as nitrogen, thus pointing to an oxidation phenomenon.
Figure 3.72: TGA overlay of PDMS A-treated PET fibers heated at 100°C min⁻¹

Figure 3.73: DTGA overlay of PDMS A-treated PET fibers
Figure 3.74: TGA overlay of PDMS B-treated PET fibers heated at 100°C.min⁻¹

Figure 3.75: DTGA overlay of PDMS B-treated PET fibers
Figure 3.76: TGA overlay of CT205E-treated PET fibers heated at 100°C.min⁻¹

Figure 3.77: DTGA overlay of CT205E-treated PET fibers
Figure 3.78: TGA overlay of Wetsoft-treated PET fibers heated at 100°C.min⁻¹

Figure 3.79: DTGA overlay of Wetsoft-treated PET fibers
Figure 3.80: TGA overlay of AF2340-treated PET fibers heated at 100°C.min⁻¹

Figure 3.81: DTGA overlay of AF2340-treated PET fibers
Figure 3.82: TGA overlay of Powersoft-treated PET fibers heated at 100°C.min$^{-1}$

Figure 3.83: DTGA overlay of Powersoft-treated PET fibers
Figure 3.84: TGA overlay of SE26-treated PET fibers heated at 100°C.min⁻¹

Figure 3.85: DTGA overlay of SE26-treated PET fibers
The TGA curves all display the same tendencies. No significant changes in the thermal degradation behavior of polyester behavior are visible from the curves. The first step in the degradation process occurring between 400ºC and 500ºC corresponds to the simultaneous β CH-transfer reaction and depolymerization [89]. The second step occurring between 600ºC and 750ºC corresponds to the further oxidation of the residue formed during the first step and of the hydrocarbon species still present [89]. With a higher amount of finish applied on the fiber, the final amount of residue increases as the silicone compound reacts to form silicon dioxide SiO$_2$ at high temperature. The second degradation of polyester fibers is absent in nitrogen [90]. Second stage of decomposition has been attributed to the formation of chars, such as the oxidation, pyrolysis and hydrolysis residues of PET chains obtained from the first degradation step [91].

The overall trend of the TGA curves suggests that any changes triggered by the silicone-based treatment do not have a significant impact on the thermal degradation behavior of polyester fiber. More striking differences may possibly be observed at a lower heating rate, as described by Cooney et al. [92]. However, by doing so we would move even further from the reality of an actual flame test.

3.3.1.2 Thermograms of spunbond polyester samples treated with non- silicone based finishes

The same stages can be observed during the thermal degradation of SR-treated polyester fibers in Figure 3.86 and Figure 3.87, with no major effect from the finish.
Figure 3.86: TGA overlay of SR-treated PET fibers heated at 100°C.min⁻¹

Figure 3.87: DTGA overlay of SR-treated PET fibers
### 3.3.2 Data extracted from the DTGA thermograms

Several steps in the thermal degradation process can be highlighted from the TGA curves. The temperature at which the first 5% weight loss occurred was used \((T_{5\%})\) since it is less sensitive to sample size, as described by Cullis et al. [88]. This temperature can be considered as the temperature of initial significant degradation. In order to retrieve more information, a plot obtained from the temperature derivative of the weight loss signal was generated (DTGA). The temperatures for the maximum rate of decomposition \(T_{\text{max}}\) and the maximum rate of decomposition in \%\text{.min}^{-1}(\text{Rd}_{\text{max}})\) were found at the maxima of the DTG curve. The % weight loss was also recorded at that point. The TA Universal analysis software provided the % weight losses corresponding to the two major steps of the thermal degradation process using step signal.

The temperatures listed in Table 3.7 display a narrow window for when the rate of degradation reaches a maximum, which occurs near 475°C despite the large differences in % add-on levels. Similarly, \(T_{5\%}\) values listed in Table 3.8 show little variation from untreated polyester fibers. For a greater amount of finish present on the fabric, lower temperatures can be attributed to less thermally stable water dispersed finishes releasing volatiles a few degrees earlier than PDMS A for instance.
Table 3.7: Temperature (°C) at maximum rate of decomposition ($T_{\text{max}}$)

<table>
<thead>
<tr>
<th>Finish</th>
<th>% owf</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1%</td>
</tr>
<tr>
<td>PDMS A</td>
<td>473</td>
</tr>
<tr>
<td>PDMS B</td>
<td>474</td>
</tr>
<tr>
<td>Powersoft</td>
<td>477</td>
</tr>
<tr>
<td>Wetsoft</td>
<td>474</td>
</tr>
<tr>
<td>SE26</td>
<td>474</td>
</tr>
<tr>
<td>CT205E</td>
<td>474</td>
</tr>
<tr>
<td>AF2340</td>
<td>469</td>
</tr>
<tr>
<td>SR</td>
<td>469</td>
</tr>
<tr>
<td>Untreated PET fibers</td>
<td>470</td>
</tr>
</tbody>
</table>

Table 3.8: Temperature (°C) at initial degradation (5% weight loss)

<table>
<thead>
<tr>
<th>Finish</th>
<th>% owf</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1%</td>
</tr>
<tr>
<td>PDMS A</td>
<td>421</td>
</tr>
<tr>
<td>PDMS B</td>
<td>419</td>
</tr>
<tr>
<td>Powersoft</td>
<td>421</td>
</tr>
<tr>
<td>Wetsoft</td>
<td>423</td>
</tr>
<tr>
<td>SE26</td>
<td>422</td>
</tr>
<tr>
<td>CT205E</td>
<td>423</td>
</tr>
<tr>
<td>AF2340</td>
<td>423</td>
</tr>
<tr>
<td>SR</td>
<td>417</td>
</tr>
<tr>
<td>Untreated PET fibers</td>
<td>421</td>
</tr>
</tbody>
</table>
3.3.2.1 Weight losses in main degradation

As discussed earlier, the two distinguishable degradation steps both result in substantial weight losses. Figures 3.88 through 3.95 show these two weight losses stacked with final residues for each finish.

The weight losses gathered from the TGA curves do not show any significant difference between treated and untreated fibers. The first step in the degradation process fluctuates as the amount of finish on the fibers increases. Similarly, the much slower second transition in the degradation process shows little difference between the types of treatments. The residual mass could be due to excessive charring of the polyester sample because of the silicone add-on as suggested by Swihart et al. in their TGA trials [74]. However the following charts suggest that the final amount of residual degraded silicone stems from variation from the overall fabric % add-on.

% Weight losses and residues of PDMS A-treated PET fibers

Figure 3.88: TGA % weight losses and residue of PDMS A-treated fibers vs. % owf
% Weight losses and residues of PDMS B-treated PET fibers

Figure 3.89: TGA % weight losses and residue of PDMS B-treated fibers vs. %owf

% Weight losses and residues of CT205E-treated PET fibers

Figure 3.90: TGA % weight losses and residue of CT205E-treated fibers vs. %owf
% Weight losses and residues of Wetsoft-treated PET fibers

Figure 3.91: TGA % weight losses and residue of Wetsoft-treated fibers vs. %owf

% Weight losses and residues of AF2340-treated PET fibers

Figure 3.92: TGA % weight losses and residue of AF2340-treated fibers vs. % owf
% Weight losses and residues of Powersoft-treated PET fibers

![Graph showing % weight losses and residues of Powersoft-treated PET fibers vs. % owf.]

Figure 3.93: TGA % weight losses and residue of Powersoft-treated fibers vs. % owf

% Weight losses and residues of SE26-treated PET fibers

![Graph showing % weight losses and residues of SE26-treated PET fibers vs. % owf.]

Figure 3.94: TGA % weight losses and residue of SE26-treated fibers vs. % owf
% Weight losses and residues of SR-treated PET fibers

![Graph showing weight losses and residues of SR-treated fibers vs. % owf.](image)

*Figure 3.95: TGA % weight losses and residue of SR-treated fibers vs. % owf*

### 3.3.2.2 Maximum rate of degradation

From the DTGA curves, the maximum rate of degradation can be plotted against the % owf applied to the polyester fibers. The general trend is a decrease in the maximum rate of thermal degradation as the amount of finish present on the polyester fibers increases. This can be explained by the thermal stability of silicone finishes, compared to polyester, thus slowing down the maximum rate of the system. However, the silicone finish does seem to act as a thermal shield since that degradation occurs within a very narrow range of temperature regardless of the % owf applied. The difference in maximum rate of degradation suggests the action of the finish on the release of volatiles from the polyester fibers.
% Mass loss at Maximum rate of degradation vs. % owf

Figure 3.96: % Mass loss at maximum rate of degradation of PDMS A-treated PET fibers vs. % owf

% Mass loss at Maximum rate of degradation vs. % owf

Figure 3.97: % Mass loss at maximum rate of degradation of PDMS B-treated PET fibers vs. % owf
Figure 3.98: % Mass loss at maximum rate of degradation of CT205E-treated PET fibers vs. % owf

Figure 3.99: % Mass loss at maximum rate of degradation of AF2340-treated PET fibers vs. % owf
% Mass loss at Maximum rate of degradation vs. % owf

Figure 3.100: % Mass loss at maximum rate of degradation of Powersoft-treated PET fibers vs. % owf

% Mass loss at Maximum rate of degradation vs. % owf

Figure 3.101: % Mass loss at maximum rate of degradation of Wetsoft-treated PET fibers vs. % owf
In the specific case of PDMS A-treated polyester fibers, the TGA analysis shows that the maximum rate of decomposition tends to decrease when the amount of coating increases. The PDMS coating slows the thermal degradation process by acting as a thermal insulator. At lower concentrations, the maximum rate of decomposition is much closer to the rates observed in uncoated fibers. However $T_{\text{max}}$ remains in the same 10 degrees window, between 469°C and 479°C for both coated and uncoated fibers. The samples retain a stable mass up to 380°C regardless of the concentration; untreated fibers show the same behavior. The PDMS treatment does not affect the onset thermal stability of polyester fibers in air. Similar conclusions can be drawn from the other types of finishes.

Figure 3.102: % Mass loss at maximum rate of degradation of SE26-treated PET fibers vs. % owf

In the specific case of PDMS A-treated polyester fibers, the TGA analysis shows that the maximum rate of decomposition tends to decrease when the amount of coating increases. The PDMS coating slows the thermal degradation process by acting as a thermal insulator. At lower concentrations, the maximum rate of decomposition is much closer to the rates observed in uncoated fibers. However $T_{\text{max}}$ remains in the same 10 degrees window, between 469°C and 479°C for both coated and uncoated fibers. The samples retain a stable mass up to 380°C regardless of the concentration; untreated fibers show the same behavior. The PDMS treatment does not affect the onset thermal stability of polyester fibers in air. Similar conclusions can be drawn from the other types of finishes.
3.3.3 Expected residue

One way to look at the effect (or lack thereof) of the interaction between the silicone treatment and the PET on thermal degradation would be to compare the actual residue of a treated fiber to the theoretical amount of residue expected if the finish and the fiber were degraded separately. That is, that the finish and the polyester fiber do not interact. In fact, one assumption was that once silicone treated, PET fibers would char, thus leaving a large amount of residue compared to untreated fibers. Assuming that the fibers selected for thermal degradation are a representative sample of the treated fabric, we can calculate the theoretical amount of finish present in the fiber sample and compute the expected residue as an aggregate of the finish residue and untreated fibers residue.

The mass of a sample of treated fibers can be seen as

\[ M_{T,Fib} = M_{Fin} + M_{Pet} \] (17)

Where

- \( M_{T,Fib} \) = mass of a sample of treated polyester fibers
- \( M_{Fin} \) = mass of finish present in a sample
- \( M_{Pet} \) = mass of untreated polyester fibers in a sample

Let us assume that

\[ M_{R,T,Fib} = M_{R, Pet} + M_{R, Fin} \] (18)

Where

- \( M_{R,T,Fib} \) = mass of residue left after thermal degradation of treated polyester fibers
$M_{R, \text{Pet}}=$ mass of residue left after thermal degradation of untreated polyester fibers

$M_{R, \text{Fin}}=$ mass of residue left after thermal degradation of finish

Equation (19) shows the computed percentage of residue after thermal degradation of treated polyester fibers, % $R_C$.

$$\% R_C = \frac{M_{R, T \text{ Fib}}}{M_{T \text{ Fib}}} \times 100$$ (19)

Which can be expressed as

$$\% R_C = \frac{M_{R, \text{Pet}} + M_{R, \text{Fin}}}{M_{T \text{ Fib}}} \times 100$$ (20)

Since

$$M_{R, \text{Pet}} = \% R_{\text{Pet}} \times M_{\text{Pet}}$$ (21)

$$M_{R, \text{Fin}} = \% R_{\text{Fin}} \times M_{\text{Fin}}$$ (22)

Where

$\% R_{\text{Pet}} =$ percentage of residue obtained from thermal degradation of untreated polyester fibers

$\% R_{\text{Fin}} =$ percentage of residue obtained from thermal degradation of finish

Keeping in mind that

$$M_{\text{Pet}} = \frac{M_{T \text{ Fib}}}{1+\% \text{ add-on}}$$ (23)

and

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\[ M_{\text{Fin}} = \frac{M_{T,\text{Fib}} \times \% \text{ add-on}}{1 + \% \text{ add-on}} \]  

we can compute

\[ \% R_C = \frac{\% R_{Pet} + (\% R_{\text{Fin}} \times \% \text{ add-on})}{1 + \% \text{ add-on}} \times 100 \]  

However, \( \% R_{\text{Fin}} \) has to be modified for finishes dispersed in water since the percentage of residue provided by the TGA software is based on the total mass of the sample, including water. Consequently, for finishes CT205E, SE26, Powersoft, AF2340 and SR, equation (26) is used to compute \( \% R'_{\text{fin}} \) in lieu of \( \% R_{\text{fin}} \) with:

\[ \% R'_{\text{Fin}} = \frac{M_{R,\text{Fin}}}{M_{\text{Fin Sample}} - M_{\text{solvent}}} \times 100 \]  

Where

- \( M_{\text{fin Sample}} \) = Mass of sample used for thermal degradation of finish only
- \( M_{\text{solvent}} \) = Mass of solvent removed

We can now compare \( \% R_C \) to the experimental percentage of residue \( \% R_E \) obtained from the TGA. The absence of noticeable difference between the computed residues and the experimental ones would then suggest the absence of charring effect from the silicone treatment during the thermal degradation.
PDMS A-treated PET fibers residue

Figure 3.103: Experimental and computed residues of PDMS A-treated fibers vs. % owf

PDMS B-treated PET fibers residue

Figure 3.104: Experimental and computed residues of PDMS B-treated fibers vs. % owf
Figure 3.105: Experimental and computed residues of CT205E-treated fibers vs. % owf

Figure 3.106: Experimental and computed residues of Powersoft-treated fibers vs. % owf
Wetsoft-treated PET fibers residue

![Wetsoft-treated PET fibers residue graph]

*Figure 3.107: Experimental and computed residues of Wetsoft-treated fibers vs. % owf*

AF2340-treated PET fibers residue

![AF2340-treated PET fibers residue graph]

*Figure 3.108: Experimental and computed residues of AF2340-treated fibers vs. % owf*
Figure 3.109: Experimental and computed residues of SE26-treated fibers vs. % owf

Figure 3.110: Experimental and computed residues of SR-treated fibers vs. % owf

SE26-treated PET fibers residue

SR-treated PET fibers residue
Figures 3.103 through 3.110 display the differences between theoretical and experimental residues for the finishes used. These charts suggest that the interaction between the silicone finish and the polyester fiber does not result into an excessive amount charring which would translate into a suppression of the melt dripping behavior in a flame test. In most cases, the experimental residue appears to be slightly larger than the computed one, which can be due to the finish “protecting” the polyester fiber during the thermal degradation. In addition, since the finish tends to accumulate at cross over between fiber, the actual amount of finish present may be slightly higher than the calculated one.

3.4 Scanning Electron microscopy (SEM)

3.4.1 Examination of polyester fibers from spunbond nonwoven substrate under SEM

Untreated fibers from the spunbond fabric appear to be round shaped with a smooth surface as shown in Figure 3.111 and Figure 3.112.
Figure 3.111: SEM image of untreated PET fibers at 60x magnification

Figure 3.112: SEM image of untreated PET fibers at 300x magnification
The silicone-treated fibers keep their smooth appearance but finish accumulation can be identified by lighter spots on treated fibers, as shown in Figure 3.113. For higher % owf levels, finish accumulation occurs at fibers contact points and between close fibers, forming a bridge between them. This phenomenon can be observed at 50% owf (Figure 3.114). Much like in bonding techniques used for nonwoven fabrics, the silicone finish seems to privilege small-area and punctiform enveloping of fiber intersection points [93]. This accumulation tendency shown in Figure 3.115 can explain the lack of fabric mobility when subjected to a flame.

Figure 3.113: SEM image of 1% owf PDMS A-treated fibers at 80x magnification
Figure 3.114: SEM image of 50% owf PDMS A-treated PET fibers at 70x magnification

Figure 3.115: Schematic of finish accumulation sites on fibers
3.4.2 Scanning Electron Microscopy of TGA residues

3.4.2.1 Examination of untreated polyester fibers TGA residue under SEM

The micrographs show fragments of residue collected from TGA pans after thermal degradation conducted in air, up to 1000°C at a rate of 100°C.min⁻¹. In the case of untreated polyester fibers, the residues are more difficult to collect due to their low quantity. They appear to be very porous and ash like as shown in Figure 3.116 and 3.117.

Figure 3.116: SEM image of TGA residue of untreated PET fibers at 250x magnification
3.4.2.2 Examination of silicone-treated polyester fibers TGA residue under SEM

In the case of silicone-treated fibers, the residue appears to be made out of large white brittle pieces that have cracked due to intense heat. This phenomenon can be observed in Figure 3.118 and Figure 3.119 for the case of polyester fibers from PDMS A-treated spunbond nonwoven substrate. This behavior appears to be more pronounced at a high % owf level (50% owf).
Figure 3.118: SEM image of TGA residue of 5% PDMS A-treated PET fibers at 60x magnification

Figure 3.119: SEM image of TGA residue of 50% PDMS A-treated PET fibers at 60x magnification
3.4.2.3 Examination of silicone finishes TGA residue under SEM

A similar type of residue can be observed after thermal degradation of a silicone-based finish, such as PDMS A, as shown in Figure 3.120 and Figure 3.121. The residue appearance shows an analogous cracked pattern on a white shell generated from intense heat. The residue observed for silicone-treated polyester fibers appear to be mostly constituted of the silicone finish residues.

Figure 3.120: SEM image of TGA residue of PDMS A at 250x magnification
3.5 Elemental analysis

The main elements detected in the TGA residues are Carbon, Oxygen and Silicon. At lower levels, Antimony and Titanium are also detected. The presence of antimony can be explained by its use in the fabrication process of polyester as a catalyst agent [94]. In the same fashion, the presence of Titanium comes from TiO₂, used as a delustrant agent.

If we use the same assumptions employed to compute equation (25), we can use the amount of finish theoretically present on a fiber to compare the change in percentage of Si atoms after going under a thermal degradation. In order to do so, other assumptions must be made, such as the formulation of PDMS A. Based on the viscosity of the silicone fluid, the molecular weight can be used to estimate the percentage of Si atoms in the

Figure 3.121: SEM image of TGA residue of PDMS A at 1000x magnification
3.5.1 Specific case for PDMS A-treated PET fibers:

3.5.1.1 Atomic % calculations

If we consider the structure of PDMS A to be of the form (CH$_3$)$_3$SiO[(CH$_3$)$_2$SiO]$_x$Si(CH$_3$)$_3$, we can compute a theoretical weight percentage for Si. The atom percentage of Si could be expressed as:

\[
\text{Atomic } \% \text{ Si} = \frac{\# \text{Si}}{\# \text{Si} + \# \text{C} + \# \text{O} + \# \text{H}} \tag{27}
\]

Where

\#Si = Number of Silicon atoms in PDMS chain.
\#C = Number of Carbon atoms in PDMS chain.
\#O = Number of Oxygen atoms in PDMS chain.
\#H = Number of Hydrogen atoms in PDMS chain.

Equation (27) can be reformulated as

\[
\text{Atomic } \% \text{ Si} = \frac{(\# \text{Si})_{\text{repeat unit}} + (\# \text{Si})_{\text{end groups}}}{(\# \text{Si} + \# \text{C} + \# \text{O} + \# \text{H})_{\text{repeat unit}} + (\# \text{Si} + \# \text{C} + \# \text{O} + \# \text{H})_{\text{end groups}}} \tag{28}
\]

Since the EDX can not detect Hydrogen, in this particular case equation (28) can be simplified to equation (29)

\[
\text{Atomic } \% \text{ Si} = \frac{(x \times 1_{\text{Si}}) + 2_{\text{Si}}}{[x \times (1_{\text{Si}} + 2_{\text{C}} + 1_{\text{O}})] + 2_{\text{Si}} + 6_{\text{C}} + 1_{\text{O}}} \tag{29}
\]

\[
\text{Atomic } \% \text{ Si} = \frac{x + 2}{4x + 9} \tag{30}
\]

Equation (30) can be rewritten as
\[
\frac{x \times (1 + \frac{2}{x})}{x \times (4 + \frac{9}{x})} \quad \text{if } x \neq 0
\]  

(31)

Consequently, for \( x \) large enough,

\[
\frac{x+2}{4x+9} \approx \frac{x}{4x} \quad \text{as} \quad \lim_{x \to \infty} \frac{2}{x} = 0 \quad \text{and} \quad \lim_{x \to \infty} \frac{9}{x} = 0
\]  

(32)

Consequently for large enough molecular weights (viscosity greater than 100 cSt) end groups become negligible and the structure can be approximated to \([(\text{CH}_3)_2\text{SiO}]_x\) for calculations purposes.

The same calculations can be applied for the other elements carbon and oxygen present in the repeat unit, using the general equation for a compound with a repeat unit containing \( n \) elements \( E_i \) with \( i=1,2,\ldots,n \):

\[
\text{Atomic} \% \ E_i = \frac{\# E_i}{n}
\]  

(33)

Where

\( \# E_i \) = number of element \( E_i \) atoms having an atomic number greater than 4 [95].

The same goes for weight percentage calculations, using equation (33)

\[
\text{Weight} \% \ E_i = \frac{\# E_i \times MW_i}{(# E_1 \times MW_1) + (# E_2 \times MW_2) + \cdots + (# E_n \times MW_n)}
\]  

(34)

Where

\( MW_i \) = Molecular weight of element \( E_i \)
Table 3.9: Theoretical elemental composition of PDMS (Atomic %)

<table>
<thead>
<tr>
<th>Element</th>
<th>Atomic %</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>50%</td>
</tr>
<tr>
<td>O</td>
<td>25%</td>
</tr>
<tr>
<td>Si</td>
<td>25%</td>
</tr>
</tbody>
</table>

3.5.1.2 Elemental analyses of PDMS A and polyester fibers

Elemental analysis PDMS A

Figure 3.123: Atomic % elemental analysis of PDMS A finish pre and post thermal degradation

The elemental composition obtained for finish PDMS A prior to thermal degradation, presented in Figure 3.123, is very close to the theoretical one listed in Table 3.9 suggesting the correct assumptions were made concerning the finish composition. The post thermal degradation data is in accordance with the oxidation behavior of PDMS at
high temperatures in air, leading to the formation of silica SiO₂ [96]. In addition, Figure 3.122 shows that the silicone treatment of polyester fiber is detectable through elemental analysis.

When comparing the post thermal degradation data of PDMS A finish to the elemental composition obtained from PDMS A-treated fibers residue presented in Figure 3.125, it suggests that the composition of the treated fibers residue is very similar to the finish residue. Additionally, when compared to the data presented in Figure 3.124, the share of carbon present the elemental analysis of untreated polyester fibers post thermal degradation does not indicate an excessive charring behavior during thermal degradation.
Figure 3.124: Atomic % elemental analysis of untreated polyester fibers pre and post thermal degradation

Figure 3.125: Atomic % elemental analysis of 1% PDMS A-treated fibers and their residue after TGA
CHAPTER 4

CONCLUSION

This research investigated the effect of commercially available silicone-based finishes on the burning behavior of polyester. In retrospect, the project title may be regarded as a misnomer since the study should focus on the events leading to the ignition of the polyester substrate.

4.1 Initial study on the effect of silicone finishes on the burning behavior of polyester

The preliminary study determined that silicone finishes negatively impact the burning behavior of polyester. The degree of crosslinking achieved through heat treatment did not have a significant effect on the burning behavior of treated polyester samples. The use of FTIR proved to be valid technique when investigating the presence of silicone finishes on a polyester fabric substrate.

4.2 How silicone finishes impact the burning behavior of polyester

It was later determined that a more accurate description would refer to the response of polyester when confronted with a flame. With their film forming properties and bonding site morphologies, silicone finishes hinder the shrinking abilities of polyester fibrous substrates. The “defense” mechanism of polyester against a flame is based on the fibers ability to move freely. The heat provided by the flame transfers the necessary energy to the fibers for this mechanism to take place. Most of this transfer occurs through convection when dealing with a vertical configuration. The heat transfer
by convection provides enough heat for the fibers to shrink away and retreat to safety but not too much as it would start pyrolyzing the material and triggering an ignition. The same reasoning holds if not enough heat is transferred through convection, thus leaving the fibers in direct contact with the flame leading to a rapid ignition. In this case, the thermally stable silicone finish seems to hold the fibers in place long enough for the temperature to reach the pyrolysis threshold leading to ignition. Once the flaming combustion initiated through the burner flame, the self sustaining combustion takes place until the inherent melt dripping behavior of the polyester breaks this cycle, by flowing down along the edges of the sample holder. The heat provided by the flaming fabric is now triggering melt dripping thus moving the flame away from the remaining fabric.

In the case where ignition occurs, the phenomenon of self-extinguishment still prevails as the combustion ceases before the whole sample is consumed by the flames.

### 4.3 Thermal degradation in air

The thermal degradation of polyester fibers in air at 100°C.min⁻¹ was not significantly modified by silicone-treatment nor by the functionality of the finish. The weight losses occurring during the two major decomposition processes remain similar across the several types of finishes and their % owf.

Similarly, the temperature of initial degradation at 5% stays within a few degrees of 420°C, much like the temperature of the maximum rate of degradation, staying around 475°C for all finishes. The oxidation process taking place during the second degradation step is expected to take more time because of the amount of finish present on the fibers.
acting as a barrier, slowing down the process.

No significant interaction that would suggest a deleterious effect on the burning behavior of polyester between the finish and the fibers occurred during the thermal oxidative degradation process at 100°C.min⁻¹.

4.4 Scanning Electron Microscopy

The SEM micrographs of the treated polyester fiber showed accumulation spots of the finish at fiber intersection points or when fibers are closely packed. For lower % owf resulting in much lower % add-on, this overloading phenomenon does not seem to occur as frequently. This tendency to accumulate at these points added to their inherent film forming behavior result into a more pronounced hold on the fibers mobility. Even though a flexible film is formed upon silicone-based treatment, this film remains more thermally stable than the substrate, thus not being impacted in the temperature range where the polyester fibers display their contraction behavior. This delay in the polyester ability to contract is enough to raise the fibers temperature high enough to reach the pyrolysis stage, leading to ignition of the fabric. In order to achieve this deleterious mechanism, the treatment must achieve a good film formation as well as thermal stability in the 200°C-300°C range.

4.5 Elemental analysis

The elemental analysis of TGA residues suggests that no excessive charring occurs during the thermal degradation of polyester fibers from silicone-treated spunbond nonwoven substrate. TGA residue of silicone-treated polyester fibers appears to be
mainly constituted of silicon dioxide.

4.6 Effect of silicone finishes on the burning behavior of polyester

Even at a low % add-on level (0.1%), silicone finishes will negatively modify the burning behavior of the polyester substrate. Once that critical mass has been reached, the extent of damage sustained during a vertical flammability test will remain similar, regardless of the % owf level. The evidence suggests that the functionality of the commercial finishes used in this study has little or no effect over the degree of flammability of the treated substrate. The data suggest that the flame response of silicone-treated polyester fibers is modified through physical interactions.
CHAPTER 5

FUTURE WORK

5.1 Thermal analysis

An IR spot heater could be used to achieve comparable heating rates exhibited in the combustion of polyester when subjected to a flame [97]. For instance, it was reported that “a rapid initial heating rate of 30°C.s⁻¹ up to 400°C followed by a 25°C.m⁻¹ rate up to 500°C gave a 50% weight loss after 2 min compared to TGA where it would take almost 5 minutes on the TGA with a heating rate of 100°C.m⁻¹”.

Even though the use of differential scanning calorimetry (DSC) has been deprecated for assessment purpose under fire conditions because of its much lower heating rate compared to polymers exposed to flames, it may provide some information concerning the melting behavior during the early stages of thermal transfers to the sample [52].

The FTIR analysis could be performed during the very early stages of the thermal degradation in order to focus on the ignition process. The sample could be recovered from TGA pan at the onset degradation mark where a DTGA curve hits the 0.01°C.min⁻¹, the 1% weight loss mark and the 5% weight loss mark.

5.2 Thermomechanical analysis

The shrinking ability of polyester fibers under thermomechanical analysis (TMA) could be investigated. Even if the behavior of a single fiber under thermal distress might
not be correlatable to a full scale experiment where fibers entanglement plays a significant role in the finish distribution and in the flame response of the substrate, it could give some insight on the response of treated fibers.

5.3 **Ease of ignition**

Instead of focusing on the after-flame time described in the ASTM D6413-13, the study could focus on the ignition time by following a procedure based on ISO 6940-2004 Textile fabrics-Burning behavior-Determination of ease of ignition of vertically oriented specimen, as described by Wang et al [98].

5.4 **High-speed video camera**

The behavior of a silicone-treated spunbond nonwoven polyester substrate subjected to a non-flaming heat source in an inert atmosphere could be recorded with a high-speed video camera. The experiment would focus on the shrinking behavior of treated polyester fibers in the absence of combustion. Thus it would allow to compare the shrinking rate of untreated polyester fibers to silicone-treated ones in a nonwoven substrate.
REFERENCES


[75] Swihart, T. J.; Campbell, P. E.; Campbell, W. B. Reactive Silicones as Potential Softeners for Textile Flame Retarted Fabrics.


