

Chapter 29

Smoldering in Flexible Polyurethane Foams: The Effect of Foam Morphology

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Flexible polyurethane foams with different cell morphology (cell size and fraction of open cells) were prepared. The effect of foam morphology on smoldering was assessed. Cell-size, in combination with air permeability, appeared to be a good indicator for smoldering propensity in the range of formulations investigated here.

Introduction

Smoldering is a self-sustaining heterogeneous oxidation reaction that induces a slow, low temperature, flameless combustion. Flexible polyurethane foams (PUF) are prone to smoldering due to their high air permeability, low density and high specific surface area. Smoldering of PUF poses a serious fire hazard because

it typically yields a substantially higher yield of toxic carbon monoxide (CO) per unit mass of fuel than does flaming (though at a lower rate), and because it can initiate flaming (by transition from smoldering to flaming) with heat sources otherwise too weak (1).

Smoldering of upholstered furniture and bedding remains a threat to life and property, despite the promising introduction of Reduced Ignition Propensity cigarettes in all 50 states (2). Upholstered furniture and bedding remain the most frequent “first items to ignite” that result in residential fire deaths in the United States (3). According to estimates by the U.S. Consumer Product Safety Commission (CPSC), a large number of these fire deaths can be attributed to smoldering materials commonly found in upholstered furniture and bedding.

Smoldering in PUF has been studied extensively; however, an experimental assessment of the key parameters affecting smoldering propensity of such materials has been limited by the difficulties in obtaining foam samples with consistent and homogeneous properties (4, 5).

Numerical simulation of smoldering combustion of PUF indicated the significance of oxygen supply on the rate of smolder propagation (6–10). Thermal analysis of the foams has been performed in great detail in order to obtain multi-step models of foam pyrolysis and char oxidation that provided input data for models (8). However, morphological description of the PUF has been limited to the simplest terms.

In this study we characterize the morphology of conventional PUF (cell size, strut thickness, and open versus closed cell structure) by direct morphological indicator (*e.g.*, cell size) or indirect morphological indicators (*e.g.*, apparent density, air permeability and specific surface area) that are related to the foam morphology. Custom made batches of PUF were prepared according to the National Institute of Standards and Technology (NIST) specifications and were obtained from a commercial manufacturer (foamer). Each foam was characterized in terms of smoldering (assessed by cigarette-mockup test, see below for a description of the method) and morphology. Finally, the potential correlation between smoldering and the aforementioned morphological indicators is discussed.

Our results show that PUF foam with a largely closed-cell structure and low permeability does not smolder in the mockup test. This is in agreement with the common perception that, for natural convection smoldering, air permeability (*i.e.*, oxygen supply) is the key parameter and that smoldering always increases with air permeability (11, 12). However, for conventional foams with a largely open-cell structure and air permeability above a threshold value, smoldering appeared to be surprisingly independent of air permeability and dominated by other properties of PUF. This unexpected result shows a need for a better morphological description of the foam structure. For open-cell foams with relatively high permeability and given chemical composition, smoldering appeared to be controlled by the average cell size rather than air permeability. As a corollary, smoldering-resistant PUF can be prepared by promoting a large cell structure independently of the air permeability of the foam.

Experimental (13)

Materials

All materials were used as-received unless otherwise indicated. Commercial-grade polyether triols with a molar mass between (3000 and 3200) g·mol⁻¹ and OH number between (50.5 and 57.5) mg KOH·g⁻¹ (data provided by the manufacturer, uncertainties not available), were used. Similarly, commercial-grade organo/silicone surfactants for PUF were selected. As discussed elsewhere (14), the specific polyol and surfactant did not show any systematic significant effect on smoldering and, for sake of conciseness, are not further specified here. The other reagents used were toluene diisocyanate (TDI) (mass ratio mixture of 2,4- (80%) and 2,6-isomers (20%)), water, an amine based catalyst (DABCO **33LV**, Airproducts), a polyether based catalyst (Niax **C323**, Momentive), a tin-catalyst (Kosmos 29, **K29**, Evonik) and a fatty ester emulsifier (Addotivate **D1092**, RheinChemie).

Sample Preparation

Foam samples were prepared in a small pilot plant or in a production line by the foamer. In both cases, all reagents were pumped at a controlled rate into a fixed mixing chamber (mixing head). The pressure in the mixing head was adjusted by controlling a valve at the outlet in a range between (35 to 124) kPa. In the pilot plant, the material was transferred from the mixing head to a foaming box through a feeding tube. After 15 min at room temperature, the foams were cured in an oven at 110 °C for 1 hour and post-cured at room temperature for an additional 24 hours. In the production line, the ingredients of the foam formulation were discharged through the nozzle of the mixing head and deposited onto the front of a conveyor belt. The temperature of the foam typically reached about (150 to 170) °C in water-blown foams. Curing was completed in air, and no post-curing was required. Samples were cut with an automatic laser system. All samples were conditioned at a temperature of (21 ± 3) °C and between 50 % and 66 % relative humidity for at least 24 hours prior to testing.

Sample Characterization

Mass loss due to **smoldering** in PUFs (**ML_{Mockup}**) was measured by the upholstery cover fabric smoldering ignition resistance test (*Mockup Test*), described in the CPSC's proposed flammability standard for upholstered furniture (15), which aims to mimic a realistic ignition scenario for upholstered furniture. Briefly, two pieces of PUF are placed at right angles to one another, simulating the seat and back of a chair. The surface of the foam to be tested is covered by an upholstery fabric. A lit cigarette (Standard Cigarette for Ignition Resistance Testing, NIST SRM 1196) (16) is placed in the crevice formed by the two foam pieces, and is then covered by a piece of a standard lightweight fabric, a 100 %

cotton, white plain weave of (19 to 33) threads/cm², and areal density of (115 ± 1) g·m⁻². The test result is the mass loss of the foam specimens (after removing the charred material) during the 45 min duration of the test. A cotton upholstery fabric with consistent high smoldering (100 % cotton, indigo twill weave and an average aerial density of 445 g·m⁻² ± 3 g·m⁻²) was selected for this study and used with all foams for assessing the smoldering propensity of the foam.

The openness or porosity of PUF was described by measuring the **air permeability (Φ)**. Briefly, the volume of air flowing per unit of time through a PUF sample with a given thickness and area at a given differential pressure is measured. An electronic high differential pressure air permeability measuring instrument (FAP 5352 F2, Frazier Precision Instrument Co. Inc., Hagerstown, MD) was used in this study. Foam was cut into samples (90 x 90 x 13) mm³ and placed in a circular clamp, exposing a surface of 38.5 cm² to perpendicular air flow. The target pressure-drop through the 13 mm thick foam slice was set to 127 Pa (13 mm of water). Nozzles with orifice diameters of 1.0 mm, 1.4 mm, 2.0 mm, 3.0 mm, 4.0 mm, 6.0 mm, 8.0 mm, or 11.0 mm were used in order to reach the target pressure drop. The tests were conducted at room temperature. The values of air permeability (Φ) are expressed in terms of volumetric air flow as cubic meters per square meter of sample per min (or simply meters per min) at a temperature of 0 °C and a pressure of 100 kPa. Air permeability was measured by the foamer for all the buns (replicate foams poured per each formulation) on a foam slice collected near the center point between pour start and pour end, and at a depth of about 2.5 cm from the top surface of the foam. The foam slice was cut parallel to the bottom surface of the bun. For selected buns, multiple air permeability measurements were performed to evaluate the variation of air permeability throughout the bun.

The surface area of PUF was calculated by Brunauer-Emmett-Teller (BET) measurements (17) carried out by Micromeritics, US. The BET values of surface per unit mass of sample are then converted into mass per unit volume (specific surface area) dividing the BET values by the apparent density of the sample (ρ). The **specific surface area (SSA)** is defined here as surface per unit volume and it is expressed in inverse meters. The samples used for BET measurements were about (1 x 1 x 23) cm³.

The cell size is expressed in terms of average cross-sectional cell area measured in two-dimensional images with an area of (11.9 x 11.9) mm² and scanned by a confocal microscope (Zeiss LSM 510) with an optical thickness of 19.75 μm. For each foam location, three confocal images were acquired from orthogonal planes to account for possible anisotropy in the foam. The cross-sectional cell area in a specific foam location is calculated as the average value of cell area calculated for these three orthogonal planes. The **cell size (Σ)** for a PUF is calculated by averaging the values of cross-sectional cell area in at least three specific foam locations. Similarly, the standard deviation for Σ is calculated using the cross-sectional cell areas in multiple locations (at least three).

Image analysis of confocal images was carried out by an ImageJ plug-in (18) capable to directly segment a gray-level image using a local-maxima algorithm. A Gaussian filter blurring with a diameter of 20 pixels was applied to remove noise and prevent over-segmentation before applying the local-maxima algorithm

(noise tolerance: 2, output type: segmented particles). Finally, the ImageJ macro “analyze particle” was used for calculating the area of each segmented particle (*i.e.*, cell) that is not on the edge of the image and has a combination of area above 0.02 mm² and circularity (19) equal or above 0.75 (to remove small artifacts and minimize over-segmentation).

Table 1. Formulation identification names, number of replicates per formulation and processing conditions (uncertainties for the dosing units and pressure were not determined by the foamer)

	<i>Replicate Foams</i>	<i>K29[‡] (php)</i>	<i>H₂O (php)</i>	<i>P (kPa)</i>
F1	4	0.21	3.04	34.5
F1R	4	0.21	3.04	34.5
F2	4	0.13	3.04	34.5
F3	4	0.16	3.04	34.5
F4	8	0.16	2.95	34.5
F5	4	0.16	2.95	55.2
F6	4	0.16	2.60	34.5
F7	4	0.19	2.7	55.2
F8	4	0.16	2.7	55.2
F9	4	0.16	2.7	34.5
F10	4	0.19	2.7	34.5
F11	4	0.19	2.95	34.5
F12	4	0.19	2.95	55.2
F13	16	0.16	2.95	34.5
F14	14	0.15	2.95	48.3
F15	12	0.15	2.95	48.3
F16[*]	1	0.16	2.95	104
F17[*]	1	0.16	2.95	124
F18[†]	1	-	-	-

[‡] *Tin Catalyst.* ^{*} *Foamed on a production line.* [†] *Commercial PUF (unknown composition).*

Formulations

The formulations, processing conditions and number of replicate foams (buns) poured per each formulation are described in Table 1.

The TDI index (percentage ratio between the actual amount of TDI used in a formulation and the theoretical stoichiometric amount of TDI required to react with any reactive additive, *e.g.*, water and polyols) was kept constant at a value of 105 for all formulations by adjusting the content of TDI. The amount of each component in a formulation is expressed in parts per hundred polyols (php) (20).

The uncertainty for the dosing units and pressure were not determined by the foamer. The surfactant and polyol loadings were equal to 1 php and 100 php, respectively. The two catalysts, 33LV and C-323, were used at a constant loading of 0.06 php each. Formulations F1 to F15 were prepared in a small pilot plant (approximate bun dimensions: 0.8 m x 0.5 m x 0.2 m), formulations F16 to F17 were prepared in an industrial production line (approximate bun dimensions: 1.1 m x 1.6 m x 13.0 m). Some formulations (F4 to F14) required 0.15 php of a processing aid (D1092), due to the relatively low ambient temperature during foaming. Formulation F18 is a standard high-smoldering commercial PUF of unknown formulation, used here as an arbitrary benchmark.

Results and Discussion

Foams are three-dimensional structures containing gas bubbles (cells). In PUF, cells are polyhedrons, most closely described as dodecahedrons with pentagonal faces, separated from each other by thin sections of polymer: the foam struts (polymer at the shared edge of the polyhedrons) and the foam membranes or windows (polymeric thin film connecting the struts on a face of the polyhedron). An open-cell is a cell with only open windows, *i.e.*, no residual membrane. A closed-cell is a cell completely separated from the adjacent ones by windows. PUFs typically contain closed and open cells, as well as partially open cells (cell with few residual membranes).

PUF morphology is strongly affected by the formulation and the **processing parameters** (*i.e.*, water content, tin catalyst content and head pressure) reported in Table 1. They are routinely adjusted during PUF manufacturing to compensate for morphological variations caused by climatic conditions (*i.e.*, variations in atmospheric temperature, humidity and pressure) in order to deliver a PUF with consistent specifications throughout the year. Water is essential for the blowing action by reacting with TDI and releasing CO₂, the tin catalyst accelerates the rate of the polyol/TDI reaction, and the head pressure affects nucleation and cell growth at the exit of the mixing head (14). The cell size increased with an increase in mixing pressure and water level, and a decrease in tin catalyst. The open-/closed-cell ratio, as well as air permeability, increased with an increase in water content, and a decrease in mixing pressure and tin catalyst content (14).

Table 2. Values of density (ρ), air permeability (Φ), specific surface area (SSA) and smoldering (ML_{Mockup}). Uncertainty is shown as one standard deviation

	ρ ($\text{kg}\cdot\text{m}^{-3}$)	Φ ($\text{m}\cdot\text{min}^{-1}$)	SSA [†] ($10\cdot\text{m}^{-1}$)	ML_{Mockup} (%)
F1	30.1 $\pm$ 0.8	77.1 $\pm$ 5.2	454 $\pm$ 55	30.5 $\pm$ 12.1
F1R	28.4 $\pm$ 0.3	87.5 $\pm$ 15.2	-	0.5 $\pm$ 0.2
F2	29.1 $\pm$ 0.3	81.7 $\pm$ 5.7	-	32.0 $\pm$ 2.3
F3	28.8 $\pm$ 0.2	77.7 $\pm$ 8.6	-	29.3 $\pm$ 6.5
F4	30.1 $\pm$ 0.6	74.2 $\pm$ 8.4	-	8.1 $\pm$ 3.4
F5	30.4 $\pm$ 0.3	44.8 $\pm$ 4.1	384 $\pm$ 46	0.2 $\pm$ 0.1
F6	33.8 $\pm$ 0.8	33.4 $\pm$ 5.5	-	0.5 $\pm$ 0.2
F7	31.6 $\pm$ 0.4	4.7 $\pm$ 1.7	-	0.5 $\pm$ 0.6
F8	33.6 $\pm$ 0.5	16.6 $\pm$ 4.1	-	0.7 $\pm$ 0.2
F9	34.3 $\pm$ 0.6	59.7 $\pm$ 3.4	-	15.2 $\pm$ 5.6
F10	30.7 $\pm$ 0.7	3.1 $\pm$ 0.4	-	1.2 $\pm$ 0.5
F11	29.2 $\pm$ 0.6	43.3 $\pm$ 5.9	572 $\pm$ 69	2.5 $\pm$ 2.2
F12	28.4 $\pm$ 0.6	12 $\pm$ 12	517 $\pm$ 62	0.3 $\pm$ 0.3
F13	30.9 $\pm$ 0.9	78.4 $\pm$ 4.6	374 $\pm$ 45	21.5 $\pm$ 10.6
F14	30.1 $\pm$ 0.8	70.9 $\pm$ 10.7	300 $\pm$ 36	10.0 $\pm$ 2.5
F15	29.9 $\pm$ 0.6	78.5 $\pm$ 6.9	309 $\pm$ 37	1.2 $\pm$ 0.3
F16	26.9 $\pm$ 0.5	83.9 $\pm$ 13.3	345 $\pm$ 43	19.6 $\pm$ 5.5
F17	29.1 $\pm$ 0.4	27.9 $\pm$ 4.1	-	1.3 $\pm$ 1.0
F18	28.1 $\pm$ 0.4	-	-	28.9 $\pm$ 4.0

[†] Typical uncertainty values measured for F16.

In this study, the processing parameters were systematically varied in order to tune the properties of PUF in terms of air permeability (closed- vs. open-cell structure) and/or cell size. The density, the air permeability and the specific surface area of these PUFs are reported in Table 2. Variations for these foam properties were observed between different buns of the same formulation (bun-to-bun variability), due to intrinsic foaming repeatability limitations, and different locations in the same bun (in-bun variability), due to foam heterogeneity. The average and standard deviation for each property is reported in Table 2. Density and air permeability were measured in the same center location for each bun of formulation F1 to F15 (pilot plant foams), or in multiple locations (at least four) of the same large bun produced in the production line (formulation F16 to F18). Smoldering (ML_{Mockup}) was measured for each formulation over at least three replicate samples from one or two buns. The specific surface area

was measured for each formulation over one or two replicate measurements. A relative standard deviation of 12 % for SSA, calculated over nine repeated measurements on formulation F16, is assumed as typical standard deviation for all formulations of Table 2.

The effect of these foam properties on smoldering propensity, measured in terms of mass loss in the mockup test, is evaluated in the following sections.

Effect of Apparent Density (ρ)

The apparent density controls the net fuel load and thermal inertia of PUFs. Numerical simulation of smoldering combustion of PUF indicated an inversely proportional relationship between ρ and propagation velocity in opposed smoldering (12).

Smoldering in terms of ML_{Mockup} is plotted vs. density in Figure 1 for all formulations of Table 2. There is no suggested trend, so density does not appear to be a critical parameter for smoldering in PUF at least in the scenario and range of densities investigated here.

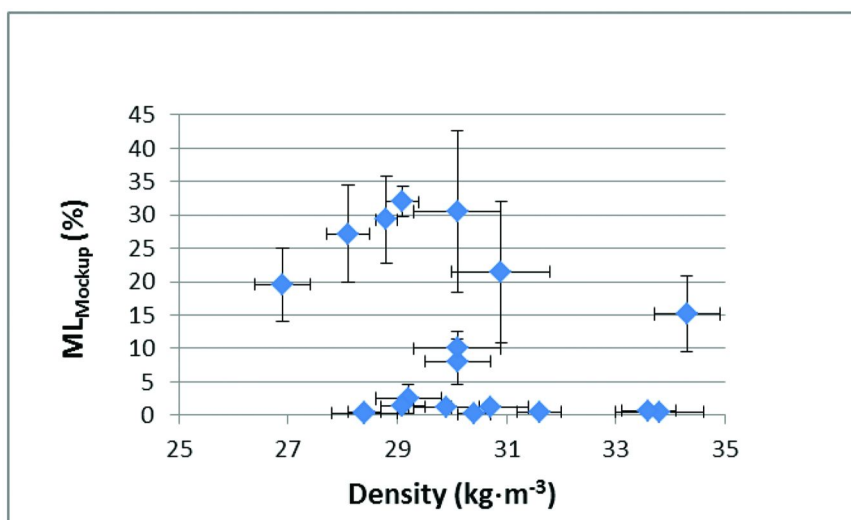


Figure 1. Values of density (ρ) vs. smoldering (ML_{Mockup}). Uncertainty is shown as one standard deviation.

Effect of Air Permeability (Φ)

Oxygen supply to the smoldering front is commonly described as the limiting factor that controls the amount of heat produced by thermal degradation of PUF. An increase in oxygen supply promotes the exothermic oxidation reaction of PUF to char (i.e., smoldering) and inhibits the endothermic pyrolytic tar formation (21). In general, oxygen transport inside a porous medium is accomplished by

diffusion and convection. In natural-convection smoldering of PUF, unless the cell structure is completely closed, oxygen transport through the foam occurs mainly by convection and the determining factor in the generation of the buoyant flow is the pressure loss through the virgin foam (11, 12). According to Darcy's law (22), the air permeability of the foam is inversely proportional to its pressure loss. These considerations suggest that, for a given PUF formulation, natural-convection smoldering increases with air permeability.

The experimental data of Figure 2, where ML_{Mockup} is plotted versus air permeability for all formulations of Table 2, show the perception that smoldering propensity increases with air permeability is too simplistic.

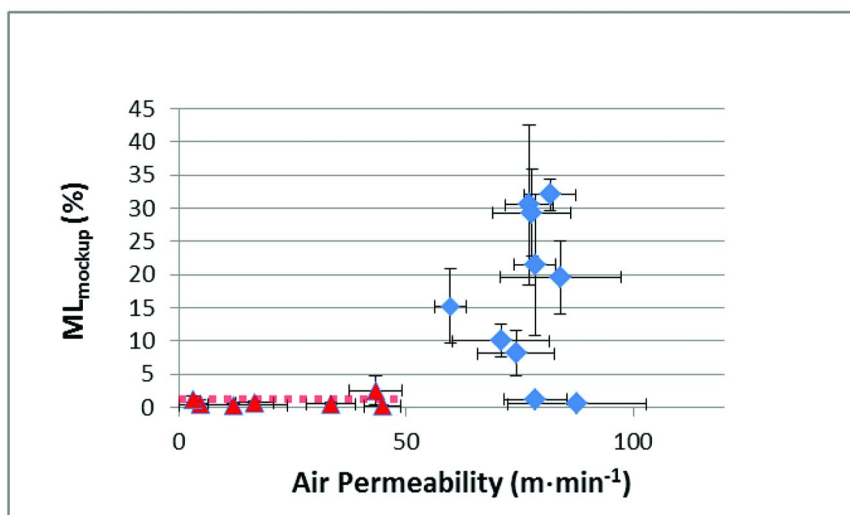


Figure 2. Smoldering versus air permeability for all formulations of Table 2. The data are split in two sets: the diamond-shaped data points (formulations with an air permeability below a threshold value $\Phi_{\text{threshold}} \approx 50 \text{ m} \cdot \text{min}^{-1}$) and the triangle-shaped data points (formulations with $\Phi > \Phi_{\text{threshold}}$). The dotted line is a least-squares regression fit to the triangle-shaped data points (uncertainty shown as one standard deviation).

Negligible smoldering (below 3 % mass loss) was observed for formulations with an air permeability below a threshold value ($\Phi_{\text{threshold}}$) of about $50 \text{ m} \cdot \text{min}^{-1}$ (triangle-shaped data points). Above this threshold value (diamond-shaped data points), there is no apparent correlation between the air permeability and smoldering. Thus, an air permeability above $\Phi_{\text{threshold}}$ is a necessary but not sufficient condition for achieving a high smoldering PUF. The data of Figure 2 are average values for a given formulation and, as previously discussed, are affected by both, in-bun variability and bun-to-bun variability.

In Figure 3, the average ML_{Mockup} measured for eight different buns of formulation F13 (at least three measurements per bun) is plotted as a function of the air permeability (one measurement per bun). Each data point is not affected by bun-to-bun variability but it is still affected by in-bun variability. The typical standard deviation due to in-bun variability for the air permeability of these buns was calculated as follow. Four buns with high air permeability ($\Phi > 70 \text{ m}\cdot\text{min}^{-1}$) were selected. For each bun, the air permeability was measured in three locations (center, pour start and pour end) and a relative standard deviation was calculated. The average value of these four relative standard deviations was used as typical standard deviation in the data of Figure 3.

Despite the large uncertainties, mainly due to the intrinsic variability of the foam properties throughout the bun, it appears that smoldering decreases when the air permeability increases. The dotted line in Figure 3 is a least-squares regression fit to the data points and has a coefficient of determination $R^2 = 0.49$. These data indicate that, at least for high values of air permeability (above $70 \text{ m}\cdot\text{min}^{-1}$) and for the formulations and smoldering scenario investigated here, air permeability is not the dominating morphological factor, and that there are parameters other than air permeability that affect smoldering.

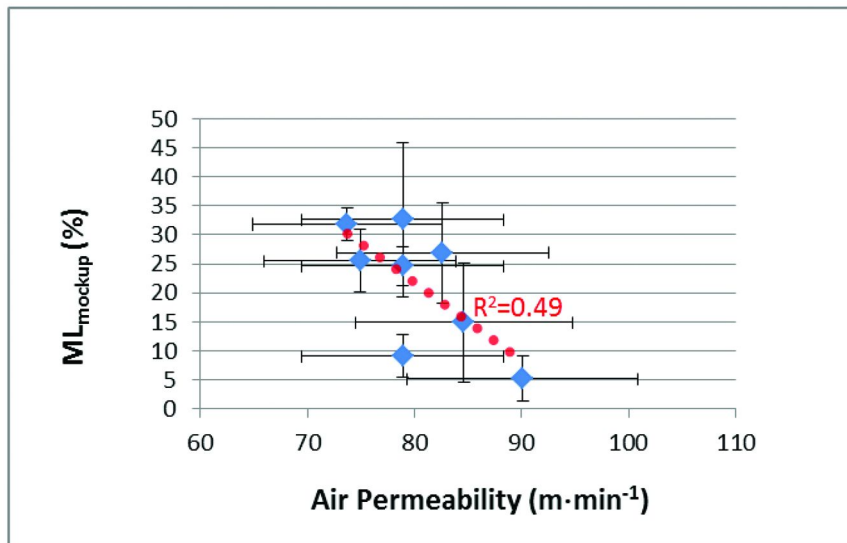


Figure 3. Average ML_{Mockup} versus air permeability for eight buns of formulation F13. The dotted line is a least-squares regression fit to the data points with a coefficient of determination $R^2 = 0.49$. Uncertainty is shown as one standard deviation.

Effect of Specific Surface Area (SSA)

The effect of SSA on smoldering is two-fold. First, smoldering is a heterogeneous reaction and, as such, the smoldering rate is expected to increase with the surface area. Second, the thermochemistry of PUF degradation is affected by SSA (23). The volume fraction of material subject to smoldering (exothermic reaction) vs. the volume fraction of material subject to pyrolysis (endothermic reaction) increases with SSA; therefore, the heat of degradation of PUF is expected to increase with SSA.

The values of SSA were measured for eight formulations of Table 2. The relative ML_{Mockup} data are plotted in function of SSA in Figure 4.

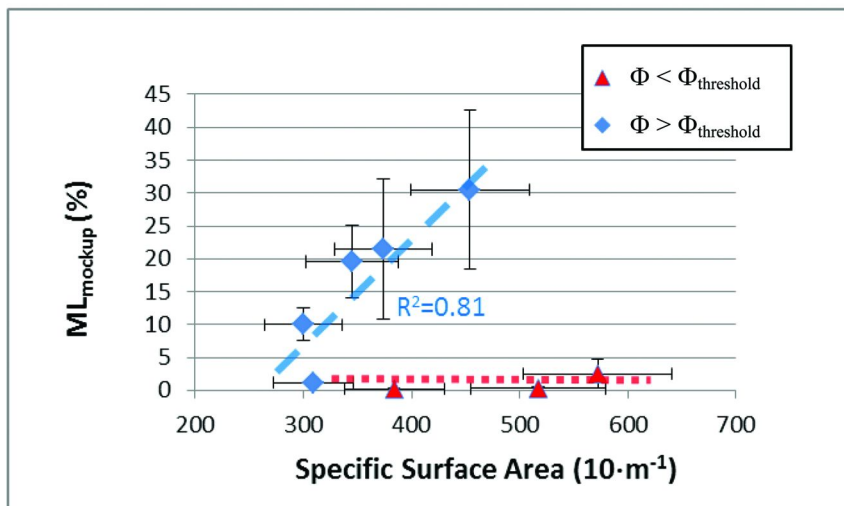


Figure 4. ML_{Mockup} versus specific surface area for eight formulations of Table 2. The dashed and dotted lines are least-squares regression fits to formulations with $\Phi < \Phi_{threshold}$ (triangle-shaped data points) and $\Phi > \Phi_{threshold}$ (diamond-shaped data points), respectively. The uncertainty is shown as one standard deviation.

The dashed and dotted lines are least-squares regression fits to the formulations with $\Phi < \Phi_{threshold}$ (triangle-shaped data points) and $\Phi > \Phi_{threshold}$ (diamond-shaped data points), respectively. The dashed line is a decent fit to the data (coefficient of determination $R^2 = 0.81$) considering the observed heterogeneity in foam properties.

These data indicate that:

- for $\Phi > \Phi_{\text{threshold}}$, SSA plays a key role in smoldering of PUF and ML_{Mockup} increases sharply with SSA (the linear fit indicates that, approximately, a 50 % increase in SSA generates a four-fold increase in smoldering);
- for $\Phi < \Phi_{\text{threshold}}$, smoldering is dominated by limited oxygen supply and $ML_{\text{Mockup}} \approx 0$ even for values of $SSA > 500 \text{ m}^{-1}$.

In completely open-cell foams, SSA is generated only by struts but, in general, SSA accounts for the surface of both residual windows and struts. An increase in the number of residual windows causes a decrease in air permeability and convective buoyancy until the point where, in a completely closed cell, oxygen transport through the foam is controlled by diffusion rather than convection. Due to the limited oxygen-supply rate, the smoldering propensity at a given SSA value for a largely closed foam ($\Phi < \Phi_{\text{threshold}}$) is lower than a largely open foam ($\Phi > \Phi_{\text{threshold}}$).

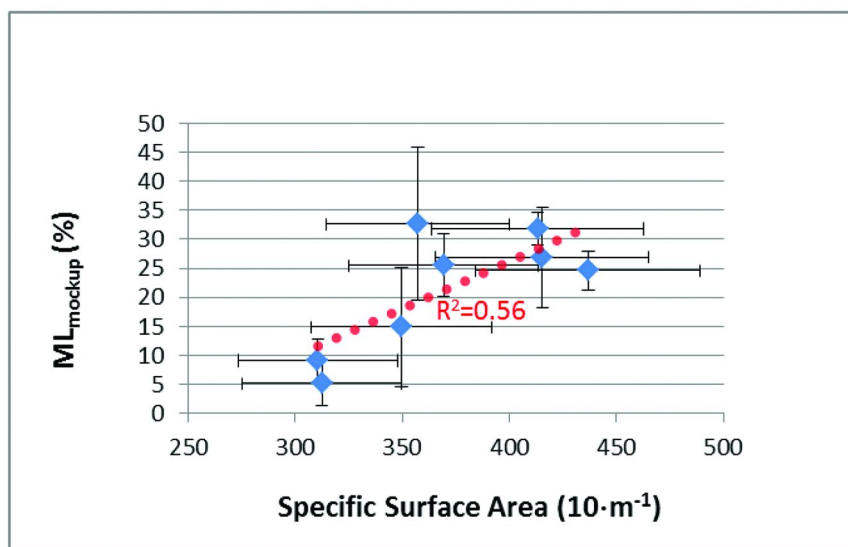


Figure 5. Smoldering (ML_{Mockup}) for eight buns of formulation F13 (same of Figure 3) as a function of the specific surface area. The dotted line is a least-squares regression fit to the data points with a coefficient of determination $R^2=0.56$ (uncertainty shown as one standard deviation).

To further support the role of SSA for $\Phi > \Phi_{\text{threshold}}$, the ML_{Mockup} data of the formulations in Figure 5 are plotted as a function of SSA (Figure 5). As already observed, there was a large scatter in these foams due to in-bun variability; however, the linear fit in Figure 5 (coefficient of determination $R^2=0.56$) indicates that smoldering increases when the specific surface area increases. Noticeably,

data of ML_{Mockup} as a function of air permeability for the same buns (Figure 3), showed that smoldering increased when air permeability decreased. These data suggest that the increase in surface area override the decrease in air permeability at least to the extent observed here.

The possible morphological implications for these phenomena are discussed in the following section.

General Considerations on Foam Morphology

The parameters considered until now (density, air permeability and specific surface area) are indirect macroscopic indicators of the foam morphology, useful to quantify microscopic features of the foam otherwise almost impossible to measure directly (*e.g.*, air permeability is used as an indicator of the fraction of open cells). In this section, samples of PUFs were observed by confocal microscopy to directly investigate the foam morphology and its possible correlation with smoldering. As an example, in Figure 6, the micrographs of one specific bun from a smoldering formulation (F13 with $ML_{\text{Mockup}} = 21.5 \% \pm 10.6 \%$, three replicates) and one bun from a non-smoldering formulation (F15 with $ML_{\text{Mockup}} \approx 1.2 \% \pm 0.3 \%$, three replicates) are compared. Samples (about 0.1 g) were collected from the center of specific bun for each of the two formulations. The values of permeability and specific surface area were measured in close proximity to these locations in order to minimize the errors induced by in-bun variability ($SSA \approx 2.6 \cdot 10^3 \text{ m}^{-1}$ and $\Phi \approx 79 \text{ m}^{-1}$ for F13; $SSA \approx 4.8 \cdot 10^3 \text{ m}^{-1}$ and $\Phi \approx 90 \text{ m}^{-1}$ for F15) (24). Noticeably, the two samples have comparable air permeabilities but substantially different specific surface area and smoldering propensity.

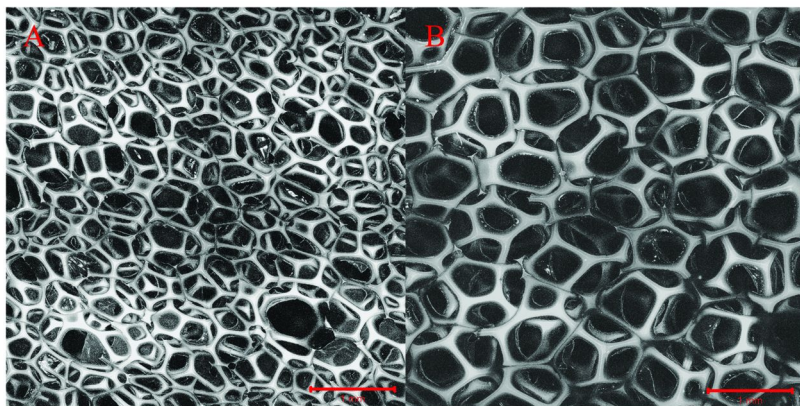


Figure 6. Confocal images for: (A) a smoldering foam ($ML_{\text{Mockup}} \approx 22 \%$) and (B) a non-smoldering foam ($ML_{\text{Mockup}} \approx 1 \%$). The smoldering foam had a smaller cell size, higher SSA and comparable air permeability ($SSA \approx 4.8 \cdot 10^3 \text{ m}^{-1}$, $\Phi \approx 79 \text{ m}^{-1}$) as compared to the non-smoldering foam ($SSA \approx 2.6 \cdot 10^3 \text{ m}^{-1}$, $\Phi \approx 90 \text{ m}^{-1}$). Bar size shown is 1 mm.

There is a large increase in cell size between the foam of Figure 6A and the foam of Figure 6B. This explains the observed increase in SSA, even though the presence of residual windows in Figure 6A might also play a role. As reported in Table 2, an increase in cell size was achieved by increasing the pressure in the mixing chamber (34.5 kPa for F15 and 48.3 kPa for F13) that controls nucleation and cell growth at the exit of the mixing head (25).

In predominantly closed-cell foams, an increase in air permeability is promoted by an increase in the fraction of open windows. In completely open-cell foams (*i.e.*, no residual closed windows), an increase in permeability can be achieved by increasing the cell size. This effect is dominant in a high permeability range where most of the cells are open. These principles are illustrated in the schematic drawing of Figure 7.

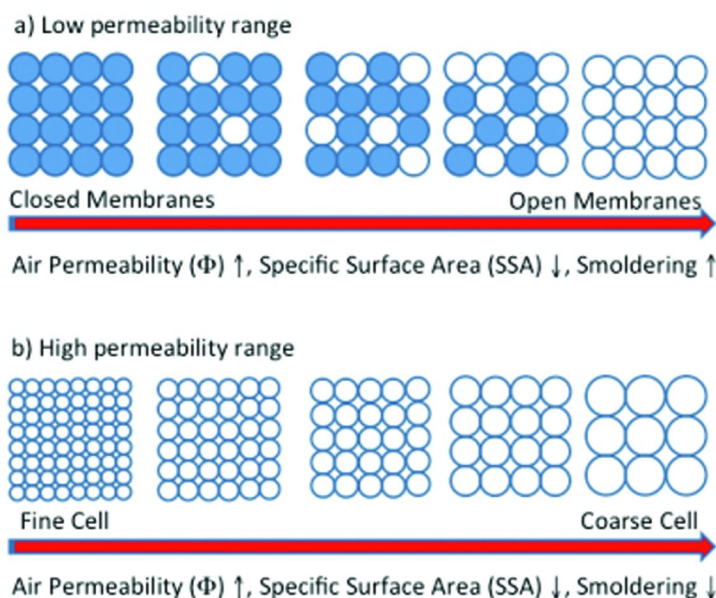


Figure 7. Schematic drawing illustrating two possible mechanisms promoting an increase in air permeability (Φ): a) increase in fraction of open membranes; b) increase in cell size. Both mechanisms induce also a decrease in SSA but only a) promotes an increase in smoldering due to an increase in oxygen supply.

Either increasing the fraction of open membranes (case *a*) or increasing the cell size (case *b*) induces an increase in air permeability and a decrease in SSA. However, smoldering increases for case *a*, due to an increase in convective buoyance (*i.e.*, oxygen supply), and decreases for case *b*, due to a reduction in SSA. For a given formulation, the morphology of the foam that maximizes smoldering is characterized by a fine and largely open cell structure with a high value of air permeability (*i.e.*, $\Phi > 70 \text{ m}\cdot\text{min}^{-1}$). A high value of Φ is necessary to promote high oxygen supply through convective movements. In this high range

of permeability a decrease in cell size promotes smoldering by increasing the amount of air/foam interface available for oxidation. This effect appears to prevail over the decrease in air permeability (*i.e.*, oxygen supply) also expected with a reduction in cell size. In general, in a typical PUF, where both open and closed cells coexist, there is no clear correlation between SSA and smoldering. This implies that SSA, by itself, is a good morphological descriptor for smoldering propensity only in fully open PUF, like reticulated PUF (26).

The cell size affects not only the specific surface area but also the heat transfer (the radiative heat transfer increase with the cell size) with possible effects on the thermochemistry of PUF degradation (27). Another potentially indirect effect of cell size on heat transfer is the reduction of strut thickness with decreasing cell size (Figure 6). The strut thickness affects the heat transfer in the foam (the ratio between conductive heat transfer over radiative and/or convective heat transfer increases with strut thickness). The contribution of each heat-transfer mode is strictly dependent on the smoldering scenario. In downward smoldering in reverse mode, for example, the convective heat flow is in the wrong direction to aid smoldering and the radiative heat transfer is equal or greater than the conductive heat transfer (28). In general, the heat transfer mode is extremely complex and dependent on the relative position to the smoldering front and smoldering scenario (1, 12). This implies that the effect of cell size on heat transfer is position dependent and hardly quantifiable.

The Effect of Cell Size

In this section, cell size measurements are used as an alternative tool to SSA for smoldering propensity assessment. Due to the bun-to-bun and in-bun variability, multiple measurements are necessary for a statistically sound approach. This is often impractical for SSA measurements because they are extremely time-consuming (several hours per test) but it is feasible for cell-size measurements (about 15 min per test).

As discussed in the previous section, the surface area of a PUF is a combination of strut-generated and window-generated surfaces. The smoldering behavior of these two types of surfaces might be different due to variations in fuel-load per unit surface area (as the thickness of a strut is approximately two orders of magnitude higher than the thickness of a window) (29), variations in the thermochemistry of decomposition (oxidation dominates pyrolysis in thin membranes) and variations in heat transfer (the ratio between conductive to radiative and/or convective heat transfer is higher in a strut due to a lower specific surface area). Cell size measurements are not affected by the fraction of closed windows, so they can be used to calculate the strut-generated surface by geometrical considerations (30).

In this study, the average cell size was measured by means of image analysis; then the effect of cell size on smoldering was considered. In general, three-dimensional imaging is required for accurate cell-size measurements, whereas, two-dimensional imaging provides an “apparent” cell-size that is a function of the optical-slice thickness.

Here, for simplicity, the cell size is expressed in terms of an average cross-sectional area per cell calculated by image analysis of two-dimensional images. The optical thickness of these images was kept constant for a proper comparison by using a confocal microscope and taking advantage of the self-fluorescence of PUF (staining is usually required to increase imaging contrast but variations in the stain penetration potentially affect the apparent cell size) (31). Image analysis was then used to identify the contour of each cell and to measure the cell area. This type of image analysis is intrinsically subject to under/over segmentation. These artifacts were minimized by using circularity filters (*i.e.*, all cells with a circularity below 0.75 were rejected).

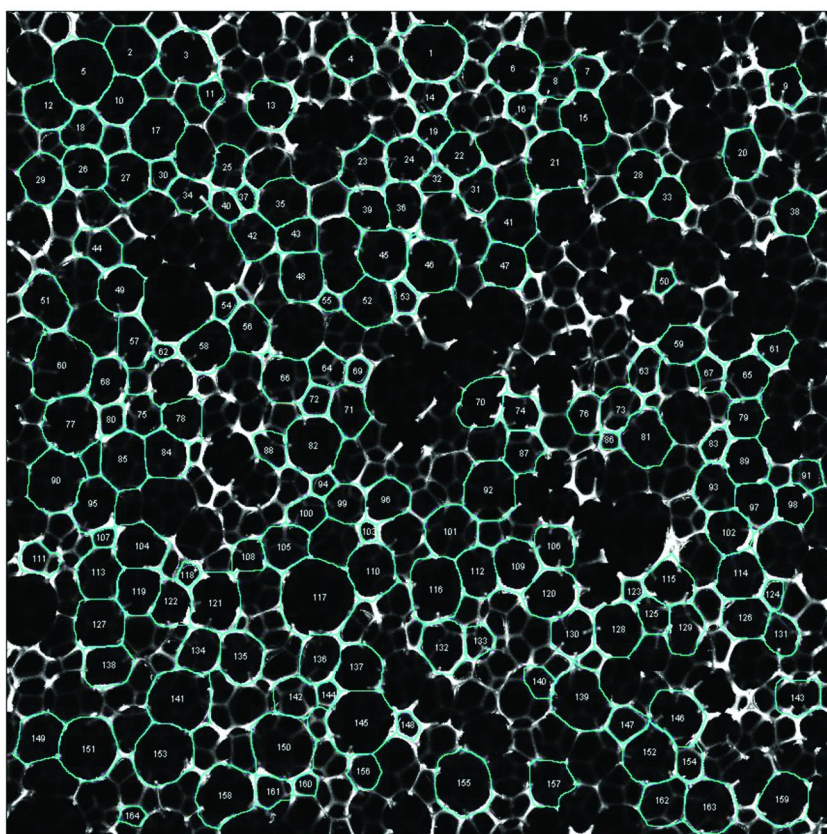


Figure 8. Confocal image for a sample of formulation F16 with highlighted contours (cyan line) for the cells identified by image analysis. (Image size: 11.9 mm x 11.9 mm).

Examples of a confocal image and image analysis are shown in Figure 8 and Figure 9. The total area of the cells identified by image analysis is only a fraction of the total area of the image (area fraction) due to the small optical thickness of the image (197.5 μm) and the circularity filter. For each foam location,

three confocal images were acquired from three orthogonal planes to account for possible anisotropy in the foam. A cross-sectional cell area in a specific foam location is calculated as an average value for the three orthogonal planes. Finally, the **cell size (Σ)** is calculated by averaging the values of cross-sectional cell areas in at least three specific bun locations. For simplicity, Σ is used as a morphological indicator for smoldering propensity without accounting for possible effects of cell-size distribution. This is considered acceptable since the average strut-area is proportional to the average cell size at a given strut thickness, unless macroscopic imperfections are observed in the cell structure (e.g., visible pits or cracks in the foam). The effect of the strut thickness on specific surface area is not accounted for in cell size measurements; it is expected that in large cell foams the observed increase in strut thickness as compared to small cell foams (Figure 6) can further decrease the specific surface area.

The values of cell size (Σ) and smoldering (ML_{Mockup}) were measured for five custom-made buns and one commercial PUF with an air permeability $\Phi > \Phi_{\text{threshold}}$. These data are plotted in Figure 10. Clearly, smoldering increases when the cell size decreases. This is mainly due to a variation of SSA, even though an effect of cell size on heat transfer might also play a role. The dotted-line curve is a power-law least-squares regression fit to the diamond-shaped data points (custom made foams) with a coefficient of determination (R^2) equal to 0.74. The power-law regression appears to be a decent fit also for the commercial formulation F18 (triangle-shaped point). These results indicate that foam morphology has a paramount importance in smoldering behavior and cell size is a good indicator of smoldering propensity for conventional PUF with $\Phi > \Phi_{\text{threshold}}$, at least for the range of formulations investigated here (impurities, such as alkali metals, are capable of enhancing smoldering) (32). Noticeably, smoldering resistance of PUFs can be enhanced by promoting a large cell size (for example, by increasing the head pressure within the processing window).

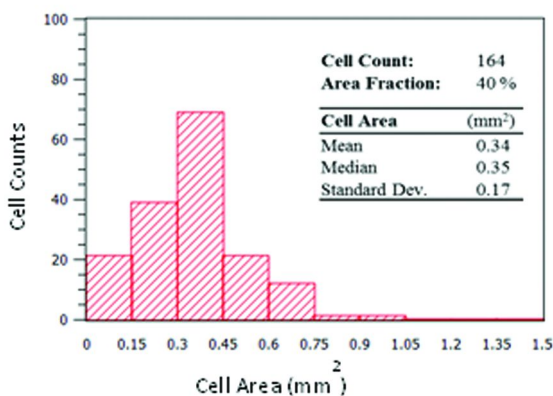


Figure 9. Histogram and basic statistical analysis for the confocal image of Figure 8.

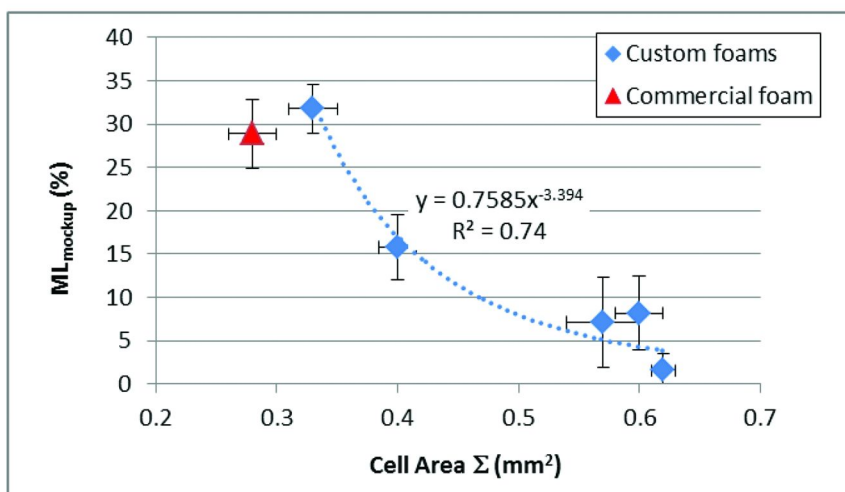


Figure 10. Smoldering propensity (ML_{Mockup}) versus cell size (Σ) for PUF with $\Phi > \Phi_{threshold}$. The dotted-line curve is a power-law least-squares regression fit to the diamond-shaped data points (custom made foams); the fitting equation and relative coefficient of determination ($R^2=0.74$) are also shown. The triangle-shaped data point is a commercial foam (F18) with unknown formulation. The uncertainties are shown as one standard deviation.

Conclusions

Custom-made, conventional, flexible polyurethane foams with large variations in air permeability and cell size were prepared and their smoldering propensity was determined. Significant variations for these foam properties were observed between different buns of the same formulation (bun-to-bun variability), due to intrinsic foaming repeatability limitations, and between different locations in the same bun (in-bun variability), due to foam heterogeneity. Multiple measurements were necessary for a statistically sound approach.

Smoldering was investigated with the *Mockup Test* that aims to mimic a realistic combustion scenario for upholstered furniture. No apparent effect of foam density on smoldering was observed in the range investigated. Negligible smoldering was observed for formulations with air permeability below a threshold value of about $50 \text{ m} \cdot \text{min}^{-1}$. Above this threshold, there was no apparent correlation between air permeability and smoldering. This is somewhat surprising because oxygen supply, that is typically the limiting factor in smoldering, increases with air permeability.

Above the permeability threshold, smoldering increased with the specific surface area. This is not surprising because smoldering is a heterogeneous oxidation reaction, and both heat and rate of reaction increases with the extent of air-foam interface. In addition, an increase in SSA promotes the exothermic

oxidation reaction of PUF to char and inhibits the endothermic pyrolytic tar formation. Below the permeability threshold, there was no effect of specific surface area and smoldering was dominated by the reduced oxygen supply.

In predominantly open-cell foams and relatively narrow range of density, the larger the cell-size, the higher the air permeability and the lower the surface available for oxidation. In addition, the cell size might affect the heat transfer mode and the thermochemistry of PUF degradation. The experimental data indicate that when the cell size decreases smoldering increases; hence, the resulting increase in surface area dominates over the decrease in air permeability, even though an effect of cell size on heat transfer might also play a role. Cell-size, in combination with air permeability, appears to be a good indicator for smoldering propensity in the range of formulations investigated here.

In conclusion, these data show that smoldering resistance of PUFs can be enhanced by promoting a large cell size (reduced surface available for oxidation) and/or a low air permeability (reduced oxygen supply).

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