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Effectiveness of Flame Retardants in TufFoam

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Abstract

An investigation of polyurethane foam filled with known flame retardant fillers including hydroxides, melamine, phosphate-containing compounds, and melamine phosphates was carried out to produce a low-cost material with high flame retardant efficiency. The impact of flame retardant fillers on the physical properties such as composite foam density, glass transition temperature, storage modulus, and thermal expansion of composite foams was investigated with the goal of synthesizing a robust rigid foam with excellent flame retardant properties.

ACKNOWLEDGMENTS

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CONTENTS

FIGURES

TABLES

1. INTRODUCTION

Rigid polyurethane foams are important synthetic materials. They are commonly used as both structural components and as potting materials for electronics. Foams can be considered as cellular solids consisting of two phases: a solid polymer phase, from which the structure of the foam is formed, and a gaseous phase. There are two types of foam structures, open-cell and closed-cell. The porous structure of the open-cell foams makes them well suited for acoustical insulation, furniture, and bedding, while closed-cell foams are better suited for thermal insulation and structural applications where strength and toughness are important properties [1]. A foam can also be a composite material incorporating fillers (metals, powders, glasses, and ceramics) into the host polymer to modify certain physical (thermal conductivity, CTE) or mechanical (modulus, strength, toughness) properties [2,3]. Typical polyurethane foams have poor flame retardancy, catching fire and remaining engulfed in flame until the fuel source is exhausted. Hence, there is a need to increase their flame retardant properties.

Flame retardants function by interfering with one of the three components that initiate and/or support combustion: heat, fuel, or oxygen. Flame retardants are generally classified according to their chemical makeup. The most common classes of flame retardants are (1) brominated, (2) phosphorous-containing, (3) nitrogen-containing, (4) chlorinated, (5) and inorganic. Bromine and chlorine interfere in the gas phase to stop the chemical chain reaction that leads to flame formation. Flame retardants containing phosphorus interrupt the combustion process by producing a layer of char on the surface of the material as phosphoric acid is released in the presence of heat. The char layer creates a barrier to the fuel source and insulates the material against further heating. Nitrogen-containing flame retardants work by forming stable by-products and a char layer when exposed to high temperatures that stop the decomposition process and prevent the release of flammable gases. They also release nitrogen gas which inhibits combustion and can act as a synergist when combined with phosphorus to provide enhanced fire protection. Inorganic compounds, most notably hydrated aluminum and magnesium oxides, are also used as flame retardants or as part of a flame retardant system. They slow down the decomposition process and release of flammable gases, release inert gases that interrupt the chemical chain reaction that produces flames, and produce a non-flammable char layer on a material's surface [4].

Liquid flame retardants such as dimethyl methylphosphonate (DMMP) can significantly improve the limiting oxygen index (LOI) of a material as it combusts. However, often it is unreasonable to increase the amount of liquid flame retardants because they can migrate to the surface of foams. Higher loadings of liquid flame retardants can also slow or retard foam formation, leading to incomplete closure of the foam cells, subsequent loss of the flame retardant, and a reduction of the flame retardancy of the foams. A range of flame retardant materials for rigid polyurethane foams have previously been explored [5, 6, 7, 8]. This study will focus on the addition of solid fillers to the foam matrix. Both solitary and combined additives were used to formulate foams with flame retardant properties. For instance, both melamine and Melapur® MP, a melamine phosphate, were tested to determine optimal flame retardancy in composite foams.

TufFoam™ was chosen as the base foam for this study. TufFoam is a rigid, TDI-free, water-blown, closed-cell, rigid polyurethane foam. It was developed with enhanced toughness and crack resistance. TufFoam, as with other rigid polyurethane foams, is extremely combustible, catching and remaining on fire until the fuel source is exhausted when exposed to open flame. In order to reduce the flammability of this foam, an array of TufFoam samples with flame retardant fillers was produced to determine the effect of the filler on the flammability of the base foam with respect to filler type, loading (wt%), and composite foam density. The materials were also characterized to determine how the filler affects the base foam properties by measuring density, storage modulus, glass transition temperature, and thermal expansion.

2. EXPERIMENTAL APPROACH

2.1. Materials

Voranol 490 and Isonate 181 were purchased from Dow Chemical in large quantities (55 gal) and decanted into smaller containers for laboratory use. DC 193 surfactant was purchased from Air Products and used as received. DABCO 33-LV catalyst was purchased from Air Products and used as received. Melapur® flame retardants were purchased from BASF and dried for 24 hours at 110 °C before use. Tetrabromobisphenol A (TBBA), melamine, triphenyl phosphine oxide, triphenyl phosphate, aluminum hydroxide, and magnesium hydroxide were purchased from Sigma-Aldrich and dried for 24 hours at 110 °C before use.

2.2. Foam Fabrication

The polyol resin side was prepared by combining Voranol 490 polyol, DC 193 surfactant, DABCO 33-LV catalyst, and deionized water, which acts as a blowing agent. The Isonate 181 modified MDI was then added to the resin mixture and the liquid was mixed for 60 seconds using a Conn mixing blade attached to a drill press. The mixing speed was adjusted to maximize mixing speed and minimize air entrapment. The sides of the mixing cup were continuously scraped with a metal spatula to ensure a homogenous foam product. The liquid was poured into a cylindrical steel mold (7.6 cm high x 15.2 cm in diameter) and a vented top (a distribution of small holes) was clamped onto the mold. The mold assembly including the vented top was internally coated with Teflon mold release and preheated to 150°F. The foam was allowed to rise, cool to room temperature for 4 hours, and then cured overnight at 150°F.

Flame retardant-filled TufFoam was formulated in an analogous method to the unfilled TufFoam detailed above. The resin-flame retardant mixture was prepared by adding previously dried flame retardant powder to the polyol/surfactant/catalyst/water mixture. The components were blended by hand until a uniform mixture was achieved (approximately 5 minutes), followed by a wet-out rest period of 15 minutes, and then a final hand mixing to ensure a homogenous mixture. The isocyanate was added to the resin-flame retardant mixture and then mixed for 60 seconds using a Conn mixing blade attached to a drill press. The foaming material was poured into a cylindrical aluminum mold and allowed to cure following the same profile as the unfilled foam.

Phosphorous-containing, metal hydroxide, melamine-based, and bromine-containing flame retardants were chosen for this study. The weight percent of flame retardant in the composite foams was varied from 0-25 wt %. The percent loading of the flame retardant added to the TufFoam was calculated according to the following equation:

$$Wt\%\ Flame\ Retardant = \frac{x}{X + Tot} \qquad (1)$$

Where:

X = the weight of the flame retardant filler

Tot = total weight of all liquid constituents

After a full cure of the foam cylinders was completed, each was cut horizontally into slices for mechanical analysis and density measurements using a band saw with a diamond abrasive blade.

The bottom of the billet was labeled slice #7 and the top was slice #1. Density was measured for each slice using the mass and volume (calculated using average thickness and diameter). DMA and TMA specimens were machined from slice 6 of each foam billet using the same band saw.

The complete list of flame-retardant fillers used is shown in Table 1. Foams were made with a base target density of 35 pounds per cubic foot (pcf) (0.56 grams per cubic centimeter) with a filler loading of 13.5 or 23.7 wt% of the total.

Table 1. Matrix of Flame Retardant Fillers Evaluated in this Report

Flame Retardant Type	Name	Supplier
Phosphorus-Containing	Triphenylphosphine oxide	Sigma - Aldrich
	Triphenyl phosphate	Sigma - Aldrich
Inorganic	Magnesium hydroxide	Sigma - Aldrich
	Aluminum hydroxide	Sigma - Aldrich
Nitrogen-Containing	Melamine	Sigma-Aldrich
	Melapur mc25 powder	BASF
	Melapur mc50 powder	BASF
	Melapur mcxl granules	BASF
Nitrogen- and Phosphorus-Containing	Melapur MP granules	BASF
	Melapur 200 powder	BASF
Brominated	Tetrabromotrisphenol A (TBBA)	Sigma-Aldrich

2.3. Foam Characterization

The full array of experimental foams was characterized in order to understand the influence that filler loading, foam density, and composite foam density have on the physical and flame-retardant properties.

2.3.1. Physical Property Measurements

For this project, the goal was to create a foam that is both strong and flame retardant. To monitor changes as fillers are incorporated into the foam, dynamic mechanical analysis (DMA) was used to monitor changes in the tensile storage modulus (E') and glass transition temperature (T_g), thermomechanical analysis (TMA) was used to measure coefficient of thermal expansion (CTE), and thermogravimetric analysis (TGA) was used to measure the rate of decomposition of the flame retardant alone and foam with flame retardant filler.

For DMA samples, specimens from each foam billet were machined using a band saw to dimensions of approximately 55 mm long x 6 mm wide x 3 mm thick. Samples were measured on the dynamic mechanical analyzer (DMA Q800, TA Instruments) using the Dual Cantilever clamp, at 20 µm amplitude and 1 Hz frequency, heating from -75°C to 250°C at a rate of 5°C/min. Measurements were performed in triplicate.

For TMA samples, specimens were machined to be approximately 6 mm square by 20 mm tall. Samples were measured on a thermomechanical analyzer (TMA Q400, TA Instruments) using the expansion probe with a heating ramp of 1°C/min, static force of 0.05 N, and a nitrogen purge at 50 mL/min. Four heating/cooling cycles from -50°C to 80°C were completed with each specimen, with a 10 minute isothermal hold at each end of the cycle. The data from the first cycle was discarded, as the material typically releases residual stress during the initial heating and cooling, and the data from cycles 2-4 were averaged for the results reported in this report. Samples were run in duplicate.

Thermal gravimetric analysis was performed using a Mettler-Toledo TGA/DSC 1. Each sample was prepared in a 70 µL alumina crucible without a lid. Samples were heated from 35 to 1000°C at 10°C/min under a flow of 20% oxygen in nitrogen at 40 mL/min. No effort was made to mix or crush either the filler or the polymer foam samples. Samples were run in triplicate.

3. EXPERIMENTAL RESULTS

3.1. Foam Fabrication

In order to determine the flame retardant properties of the composite foam, a full array of 23 foam samples was prepared with 11 flame retardant fillers (shown previously in Table 1), at two loadings each, and one unfilled foam. These samples were used to determine how the additive flame retardant affected the density of the free-rise foam and then used in initial flammability tests to down select to the flame retardant with the highest capability.

Density measurements were taken using blocks machined 25.4 mm x 25.4 mm x 50.8 mm. The densities of the foams with the addition of flame retardant fillers is listed in Table 2. It is notable that, although similar weight percentages of each of the different fillers are added to the base foam, a large variation in the final density can be seen in the final product. The effect that the filler has on final foam density is influential in the final selection of the optimal flame retardant material.

3.3. Foam Characterization

3.3.1. Flammability Testing

Flammability testing was performed using single blocks machined 25.4 mm x 25.4 mm x 50.8 mm. A flame was held to each sample for 5 and 15 seconds (Figure 1). The time to quench, percent weight loss, and any notable behavior changes or smoke generation was noted. The results of the testing can be seen in Table 2. Samples with insufficient flame retardancy at 5 seconds of flame exposure were not subjected to 15 seconds of exposure. Images for the unfilled and flame retardant filled foams after flammability testing are shown in Figure 2. The observations from these tests allowed us to down select from 11 fillers to three: Melapur MP, Melapur 200, and triphenyl phosphate. These fillers showed the most flame retardant behavior while having the least influence on the base density of the foam.

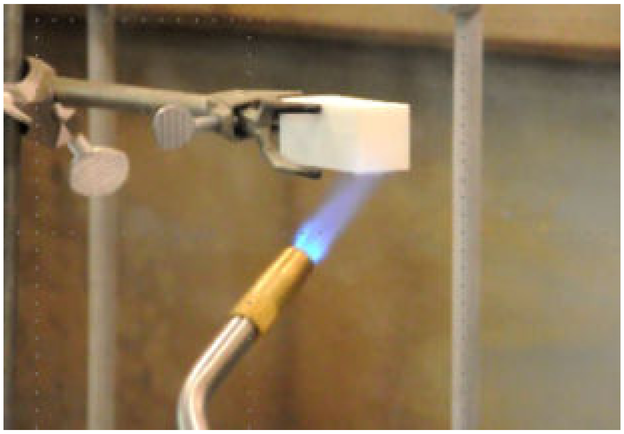
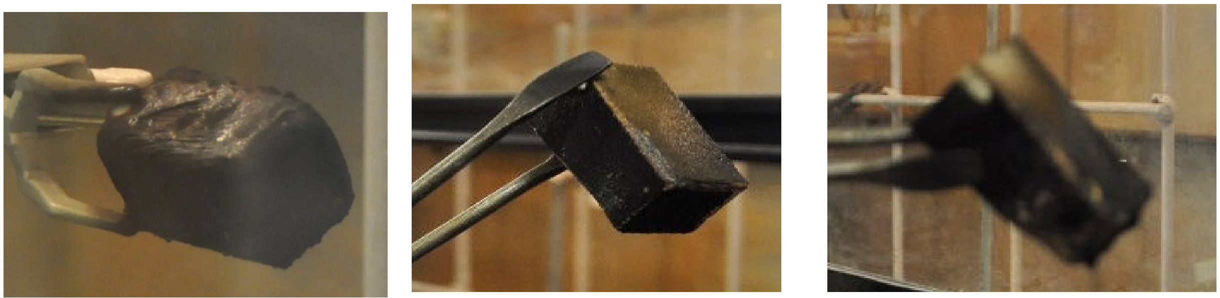


Figure 1. Flammability testing of TufFoam.

Table 2. Flame Retardant Fillers

Name	% Filler = 13.5 wt%					% Filler = 23.7 wt%				
	Final density (pcf)	**5 second burn Notes/Time to self-extinguish**	**percent weight change**	**15 second burn**	**percent weight change**	**Final density**	**5 second burn**	**percent weight change**	**15 second burn**	**percent weight change**
Unfilled TufFoam	36.4	Fully engulfed in flame, black smoke/ 4:39	12.70	None performed	-	-	-	-	-	-
Triphenylphosphine oxide	18.4	0:17	1.37	Black smoke. Sample shrunk and liquified. Noticeable shape change/ 0:40	22.90	21.15	Black smoke / 0:11	5.51	Thick black smoke/ 0:19	16.01
Triphenyl phosphate	28.55	char and smoke / 0:07	2.53	Really smoky burn / 0:17	12.08	31.8	white smoke / 0:07	1.92	Lot of black smoke / 0:19	9.23
Magnesium hydroxide	16.4	fully engulf in flame /1:44	44.24	None performed	-	11.3	Ignites, gives off yellow sparks, smokes, / 2:06	64.70	none performed	-
Aluminum hydroxide	25.7	white smoke with black ash, 6:00, slower burn than unfilled, caught fire after 5 seconds	20.62	None performed	-	26.05	caught on fire, white smoke initially, then black smoke / 2:51	8.06	2:02	14.10

Melamine	30.45	white smoke given off / 1:02	4.65	formed skin / 0:47	9.66	33.95	Formation of skin / 0:17	2.40	formed skin / 0:26	6.61
Melapur 200	21.75	(starting out is a tan color) didn't catch fire	2.06	self-extinguish immediate	5.86	19.7	white smoke / 0:08	2.48	no ignition	5.18
Melapur MC25	27.9	Caught fire, slowly burning, smoke black / 1:40	6.91	-	19.11	24.9	0:30	3.54	caught fire, white smoke / 1:32 seconds	10.78
Melapur MC50	18.45	Char / 0:45	2.93	Flamed / 1:50	18.35	18.45	Melted / 0:24	7.19	Melted / 0:57	10.49
Melapur MCXL	26.55	white smoke / 2:27	11.98	ignited, gave some white and black smoke / 1:58	20.63	24.75	1:35	10.39	light white smoke / 1:20	13.81
Melapur MP	33.1	Never caught/ immediate quench	0.86	Never caught/ immediate quench. Morphed out of shape. No smoke	2.93	33.6	white smoke, never caught/ immediate quench	0.80	never caught, immediate quench	2.93
Tetrabromo-bisphenol A (TBBA)	25.1	0:18	2.08	0:33	10.81	29.65	never caught fire	1.20	0:21	7.35



Unfilled TufFoam

Triphenylphosphine oxide
23.7 wt%
After 15 second burn

Triphenyl phosphate
23.7 wt%
After 15 second burn

Magnesium Hydroxide
23.7 wt%
After 5 second burn

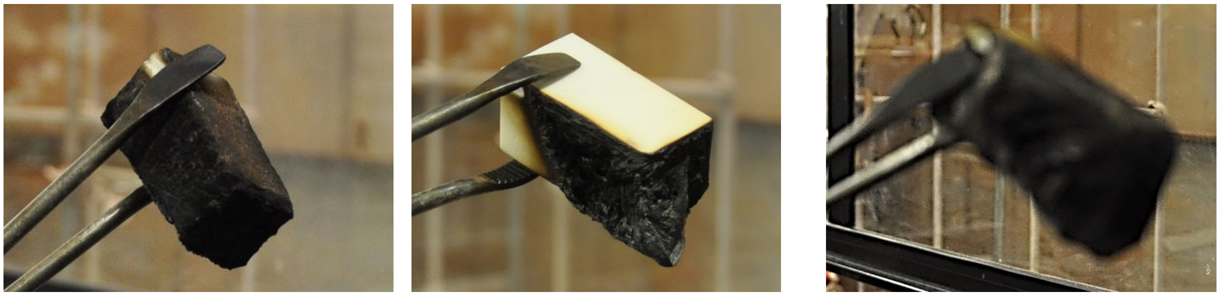
Aluminum Hydroxide
23.7 wt%
After 5 second burn

Melamine
23.7 wt%
After 15 second burn

Melapur 200
23.7 wt%
After 15 second burn

Melapur MC25
23.7 wt%
After 15 second burn

Melapur MC50
23.7 wt%
After 15 second burn



Melapur MCXL
23.7 wt%
After 15 second burn

Melapur MP
23.7 wt%
After 15 second burn

Tetrabromobisphenyl A
23.7 wt%
After 15 second burn

Figure 2. Unfilled and flame retardant filled foams after flammability testing.

3.3.2. Physical Property Measurements

Based on the results of the flammability testing, 5 foam formulations were selected for additional physical property measurements. These samples were made with a starting density of 35 pcf and contained Melapur 200 at 13.5 wt % and 23.7 wt%, Melapur MP 13.5 wt % and 23.7 wt%, and triphenyl phosphate at 23.7 wt%. Physical property measurements included measurements for storage modulus (E'), loss modulus (E"), T_g, CTE, and TGA.

The storage modulus (E') of the material corresponds to the elastic response of the material to an oscillatory force. It relates to a substance's resistance to being deformed elastically and can be related to changes in the rigid foam structure. The loss modulus (E") of the material corresponds to the viscous response of the material, and the tan delta is the ratio E"/E'. The storage modulus and tan delta curves for down-selected foam samples are shown in Figure 4, and the storage modulus values at 25°C as compared to the density values are shown in Figure 4. For all composite foams, the storage modulus increases with increasing filler loading. This trend is consistent with density as well, as increasing filler content increases composite foam density.

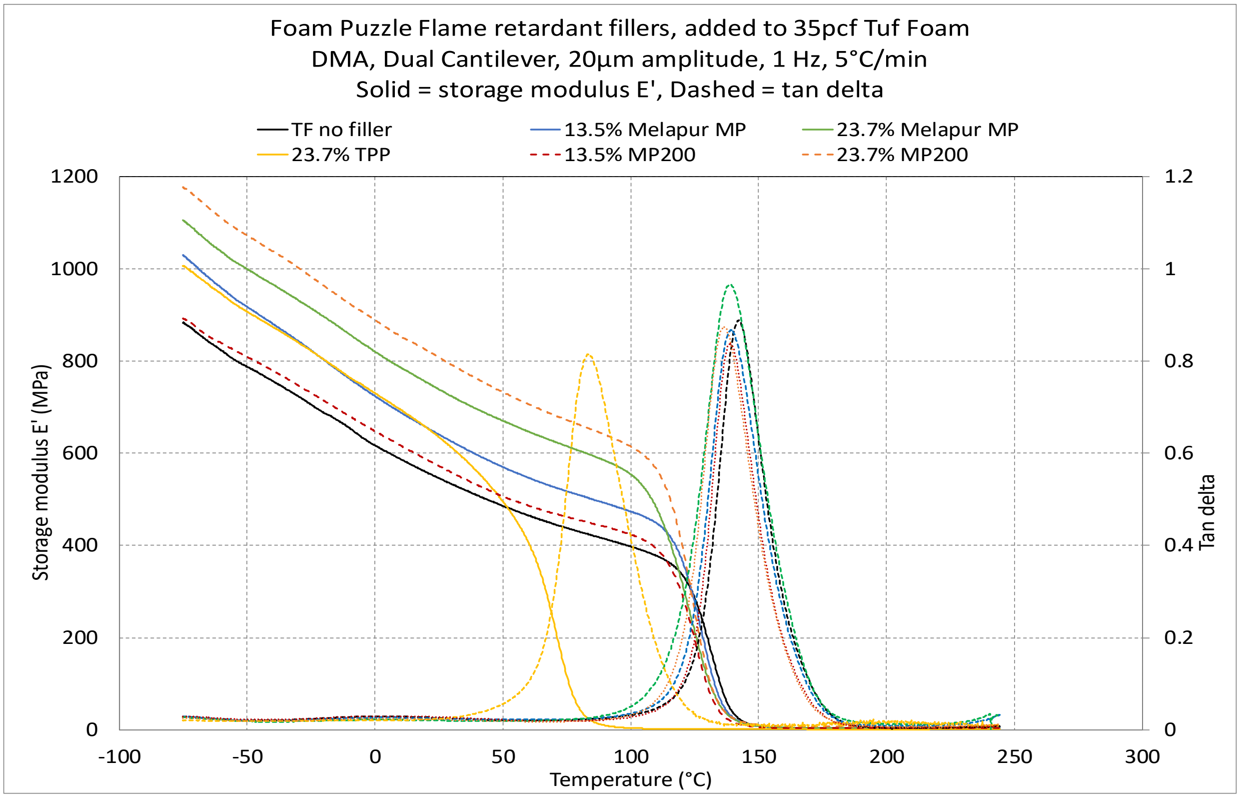


Figure 3. DMA curves showing storage modulus (E') and tan delta (E"/E').

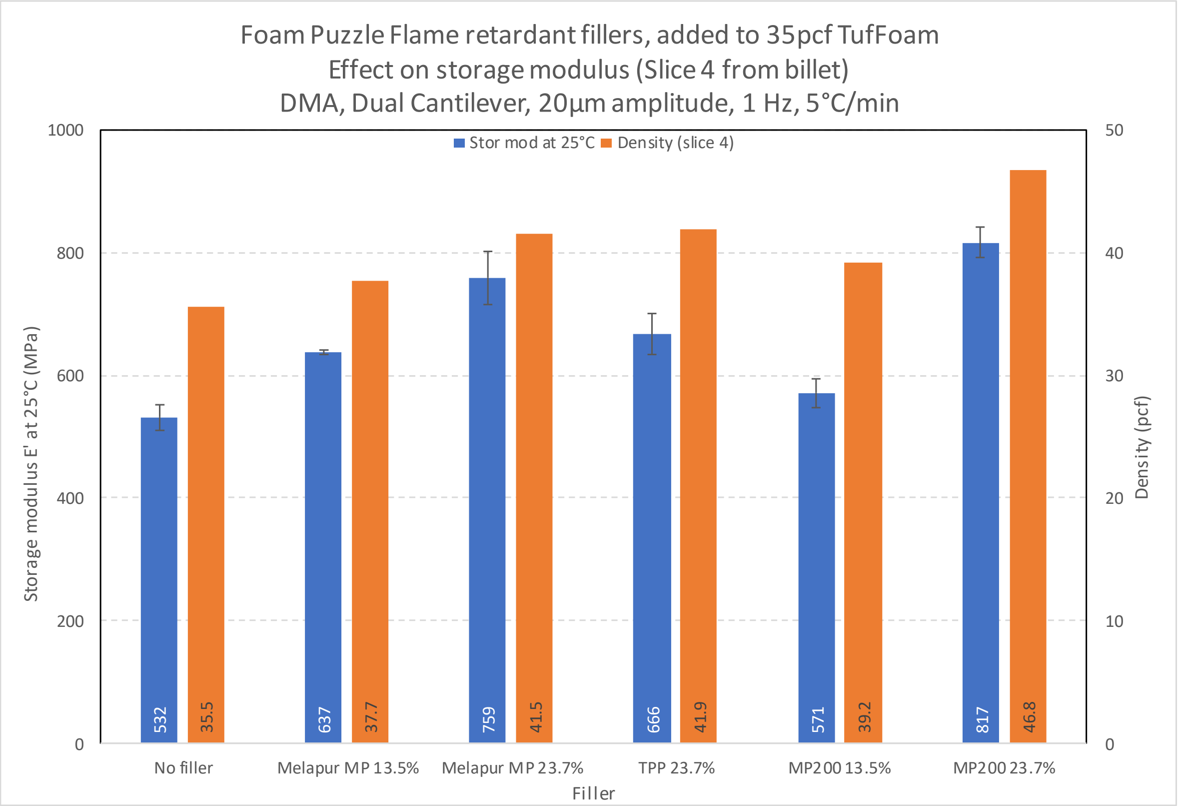


Figure 4. Storage modulus (E') data versus density for down-selected unfilled and flame retardant filled foams.

The glass transition temperature (T_g) was also examined for flame retardant filled foams as shown in Figure 5. Here, the T_g is not significantly affected by either Melapur MP or Melapur 200 but decreases significantly with the addition of triphenyl phosphate. This is significant as changes in the glass transition changes with the addition of a filler can be an indication of loss of structural integrity.

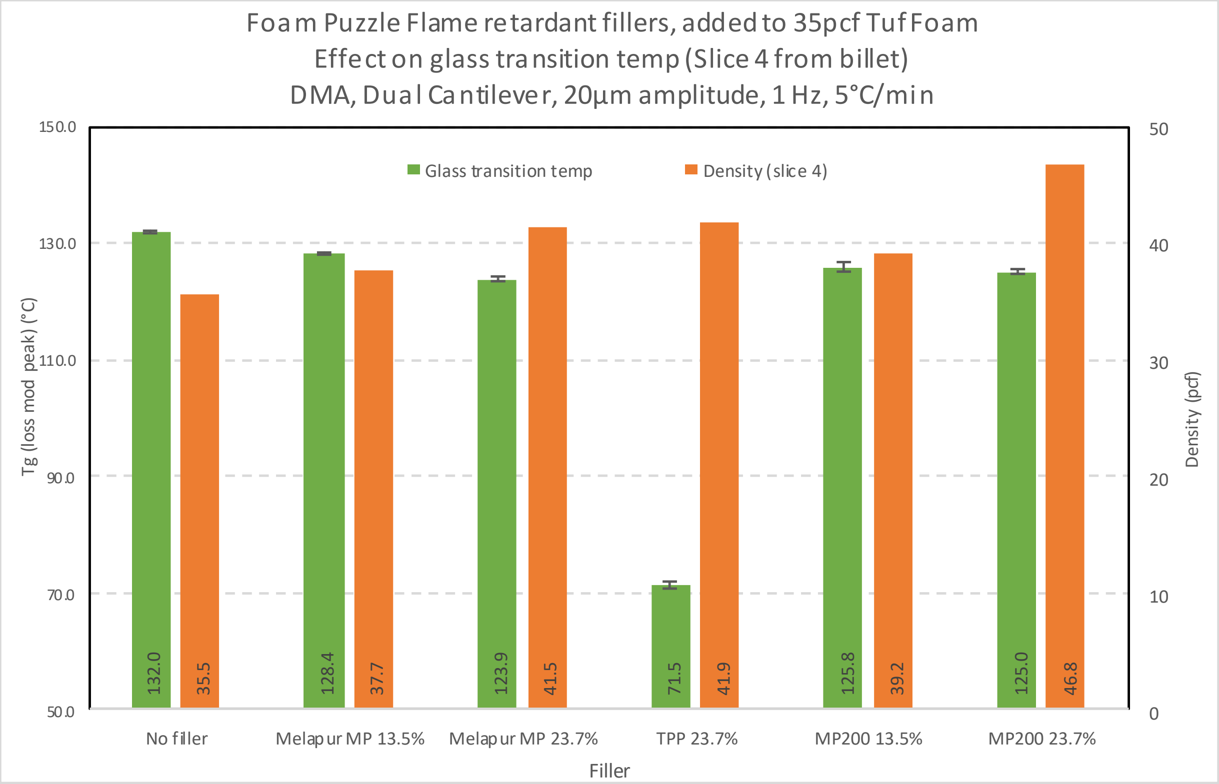


Figure 5. Glass transition temperature data versus density for down-selected unfilled and flame retardant filled foams.

The coefficient of thermal expansion (CTE) is determined to identify how the incorporation of a filler will influence the expansion or contraction of the material upon heating and cooling. Depending on the application, ideally the CTE of the foam with filler would match or lower the CTE of the unfilled foam. The CTE values for down selected composite foam samples are shown in Figure 6.

Measurements are shown for foams produced using Melapur 200, Melapur MP and triphenyl phosphate. Apart from triphenyl phosphate, the addition of fillers decreases the CTE of the TufFoam material. This is likely due to the additive material having a much lower CTE than that of the polyurethane foam. The general trend of decreasing CTE with increasing density is true for each filler tested except for triphenyl phosphate which increases the CTE significantly.

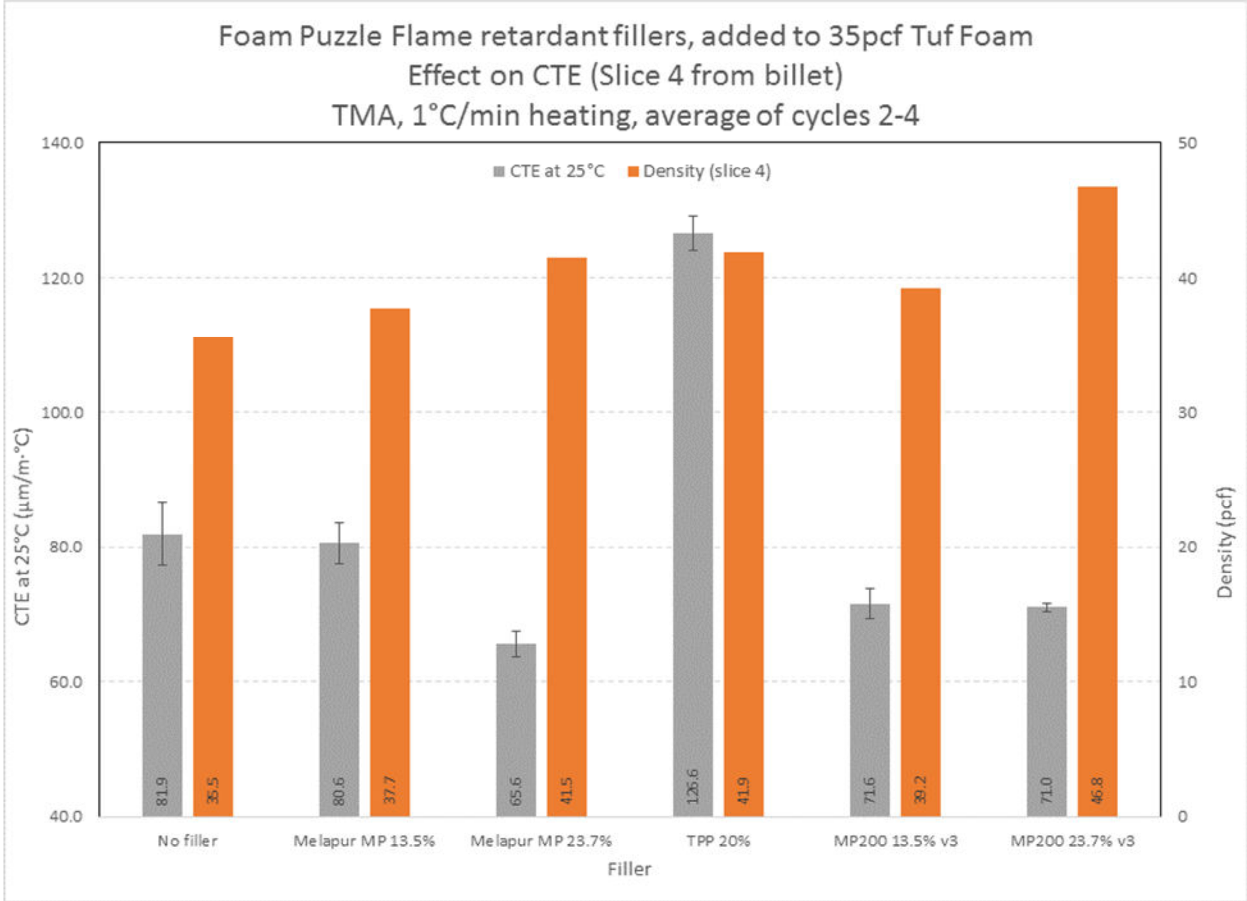


Figure 6. Coefficient of thermal expansion data vs. density for down-selected unfilled and flame retardant filled foams.

The TGA curves of the base flame retardants is shown in Figure 7 in order to observe the degradation of flame retardants under oxidative decomposition conditions. Notably, Melapur MP and Melapur 200 showed degradation behaviors that differed from the other flame retardant fillers. For these two fillers, the decomposition rate is much slower than the others chosen for this study. For these fillers, the weight loss is incomplete, indicating the formation of an intumescent char during decomposition. This effect is also noted in the TGA curves for the metal hydride additives, however in this case the final weight is likely due to residual magnesium oxide and aluminum oxide as the material decomposes when heated (Figure 8).

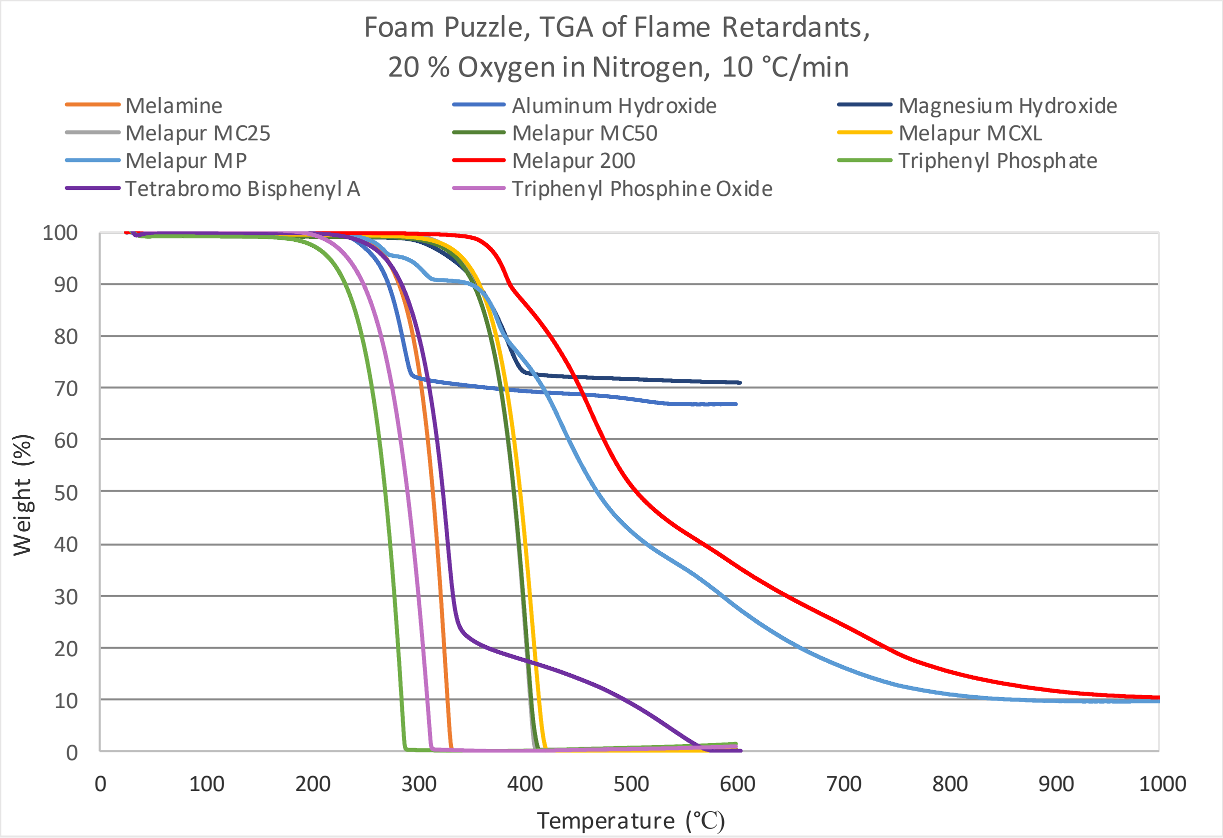


Figure 7. TGA of Flame Retardant fillers.

$$Mg(OH)_2(s) \longrightarrow MgO(s) + H_2O(g)$$

$$Al(OH)_3(s) \longrightarrow Al_2O_3(s) + H_2O(g)$$

Figure 8. Decomposition of magnesium hydroxide and aluminum hydroxide flame retardants.

The TGA curves of the foam billets with and without Melapur MP, Melapur 200, and triphenyl phosphate are shown in Figure 9. This is done to assess the effect of the addition of the fillers on the thermal stability of the foam. The decomposition of polyurethane and composite polyurethane occurs in two well-defined stages [8]. With the exception of triphenyl phosphate, the addition of fillers increases the amount of residual char remaining at the completion of the run. For most samples, the addition of flame retardant reduced the onset of decomposition and lowered the rate of weight loss from that observed in the base foam.

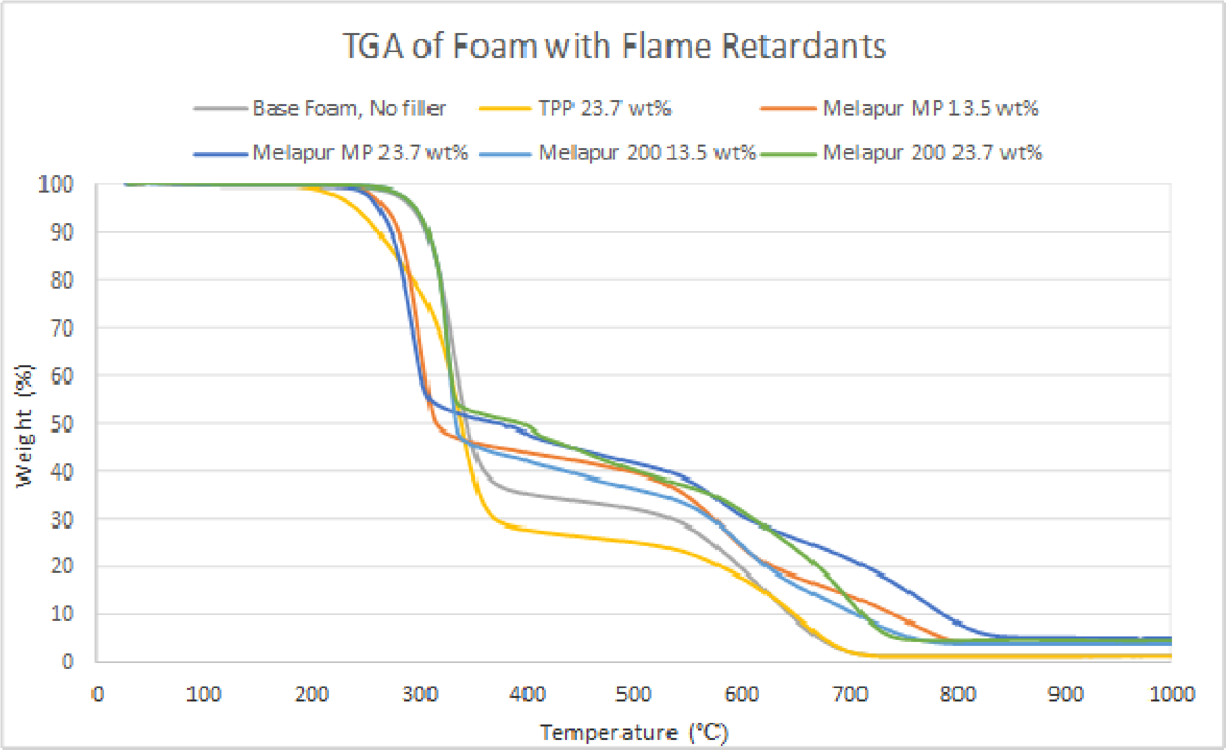


Figure 9. TGA of Flame Retardant filled foams.

4. CONCLUSIONS

A series of 23 foam samples were fabricated incorporating a range of types of flame retardant fillers in order to determine the most effective material for use in synthesizing flame retardant composite TufFoam. From these, three additives were chosen for further mechanical characterization to ensure that the addition of these fillers does not negatively impact the integrity of the foam. Physical property measurements show that the addition of Melapur MP and Melapur 200 alter the storage modulus and T_g but only slightly. Triphenyl phosphate has a significant impact on both the T_g and CTE of the foam and was eliminated as a viable option for future flame retardant foams. Both Melapur MP and Melapur 200 act effectively when added as fillers to make composite TufFoam with flame retardant properties.

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