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MECHANICAL AND FLAMMABILITY PROPERTIES OF GREEN POLYURETHANE FOAM WITH ALUMINA TRIHYDRATE AS FLAME RETARDANT

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Abstract. This paper investigates the rigid green polyurethane foam (PUF) mechanical and flammability properties when adding alumina trihydrate (ATH) as fire retardant to its composition. The rigid PUF used in this work was made of a blend of vegetable oils. The flexural stress-strain curves were obtained by the three-pointing loading flexural test, and the flammability classifications were defined according to ASTM D3801-10. The addition of ATH in different weight percentages showed different and intriguing behaviors in the PUF elasticity and flexural strengths. Until 30 wt.% of ATH, the more percentage of ATH was added into the mixture, the bigger was the decrement of the ultimate flexural strain, although, the flexural strength and elasticity modulus had non-linear behaviors with the more increment of ATH into the mixture. The ATH addition increased considerably the fire resistance of PUF when 30 wt.% was added into the mixture, although, the results from the flammability test could not classify the doped PUF with 30% ATH as determines the standard.

Keywords: Green polyurethane foam, Alumina trihydrate, Mechanical properties, Flame-retardant.

1. INTRODUCTION

The influence of the global warming dangers, the high variation of fossil fuels prices, and the concerns surrounding people about health and quality of life are important factors that raise the market for bio-based materials. Most commercial polyols used today have fossil origin and those polyols have very unstable prices. Therefore, the competitive market has enhanced the use of bio-polyols in the industry, due to its stable price and its environmental benefits (Kurańsk; 2016).

Materials combustion and flammability concerns are attached to everyone lives because of the everyday people exposure to wood, polymers, and fuels. Thus, the grown effort to combat fire or prevent it from happening has achieved many successful results. Even with those results, fire costs are approximately 1% of global gross domestic product (GDP) per year. Furthermore, polymeric materials, which are very flammable, are the most universally used materials since the 20th century (Costes, *et al.*, 2017).

Polyurethane foams (PUFs) have many different applications, such as furniture, automobile, aerospace industries, and building constructions. Most of the PUF materials found today are petro-based polyetheror polyester polyol polymerized with polyisocyanate through urethane linkages. Mineral PU products have a very harmful environmental degradation when discarded after use, and it has begun to be replaced by less prejudicial materials. Bio-based materials derived from natural oils, such as castor, palm, canola, sugar cane and soybean oils, have been used to synthesize polyols, these polyols can replace petro-based polyols as base materials in the polymerization of bio-based polyurethane foam (Zhang, *et al.*, 2014).

Polyurethane foams are macromolecules built of urethane linkages ($-NH-CO-O-$) that reaction is formed based on the polymerization of isocyanate groups with hydroxyl groups (Pillai, *et al.*, 2016). Diisocyanate reacts with the polyol creating the urethane polymer, while water reacts with some of the isocyanate groups in order to produce carbon dioxide gas. The gas gets stuck inside the mixture while the viscous liquid polymerizes and solidifies, making that stuck gas pores inside the solid polymer (Wang, 2006).

The properties of PUFs are very different depending on the density and the choice of the polyisocyanate and polyol, as well as their proportion used into the mixture. The main variations shall occur in the mechanical strength, thermal stability, and flammability of the polymer. The mechanical properties vary according to the pore sizes, shapes and quantities, being enhanced when those numbers decrease. The flammability can be reduced adding flame retardants to the mixture (Ciecierska, *et al.*, 2016; Tita, *et al.*, 2012).

Halogen, phosphorous and silicon based flame retardants are very efficient fire retardants for PUF in many applications. Although, their applications are limited due to their high necessary amount and mainly to the toxic gases liberated after their reactions (Wang, *et al.*, 2016).

Alumina trihydrate (ATH) is currently among the most used inorganic flame retardants for polymers. The benefits of using ATH are safe handling, ability to suppress smoke, generation of non-toxic fumes only, and its cost is very low compared to other flame retardants (Pei, *et al.*, 2014). The ATH mechanism that enhances flammability resistance is heat absorption by decomposition. A large volume of water is detached from ATH when certain temperature is achieved. The liberated water promotes heat absorption when it vaporizes. The presence of the vapor in the air reduces the O_2 concentration while the refractory oxide Al_2O_3 acts like a protecting layer on the substrate surface. Some problems using ATH are the maximum temperature of 200°C that it can be exposed, and the necessary high mass needed to achieve a good fire resistance, that high amount can prejudice mechanical and electrical properties (Pinto, *et al.*, 2000).

Therefore, the aim of this work was to examine and determine the effectiveness of ATH as flame retardant in the polyurethane foam, as well as the mechanical properties changes of PUF with different amounts of ATH in determined density and the same time of curring. It also analyses differences in the foam structure when ATH is added.

2. EXPERIMENTAL PROCEDURE

The blend of vegetable oils polyurethane foam raw materials KT1106/KT1106-R were kindly supplied by Kehl Indústria e Comércio Ltda. The alumina trihydrate was generously offered by Alcoa Corporation.

2.1 Manufacturing

The PUF samples were produced by mixing isocyanate and polyol in a beaker and adding ATH in some mixtures, the proportion of each reagent was 1.2:1 respectively.

The ideal density for PUF was set by analyzing the sizes of the pores as well as their quantities. The best number was selected by choosing the smallest density with invisible pores to the naked eye.

The amount of alumina trihydrate in each sample was proportional to the weight of PUF being added in percentages. The total sample weight and density was increased as more ATH was added into the mixture. However, the polymer weight in the material remained the same.

Table 1 shows the weight of each component, the weight of ATH, the air humidity, and the temperature at the time the samples were produced. The samples were named according to their ATH proportion in percentage followed by the abbreviation Flex for the flexural tests specimens and Flam for the flammability test samples.

Table 1. Component weights, air humidity, and temperature.

Samples	Isocyanate (g)	Polyol (g)	ATH (g)	Air humidity (%)	Temperature (°C)
0 Flex	24	20	0	48	18.8
10 Flex	24	20	4.4	51	17.1
20 Flex	24	20	8.8	50	18.3
30 Flex	24	20	13.2	43	17.8
0 Flam	19.8	16.5	0	42	22.4
10 Flam	19.8	16.5	3.63	42	25.1
20 Flam	19.8	16.5	7.26	44	23.2
30 Flam	19.8	16.5	10.89	72	20.8

The ideal density differs from the real density because some material remains in the beaker after the mixture is placed inside the mold. After the insertion of PUF, the molds were closed for two hours at room temperature to achieve the PUF full expansion.

2.2 Flexural Test

Flexural tests were made in the material in order to evaluate the mechanical properties of the pure polyurethane foam and with the alumina trihydrate addition.

The standard ASTM D790-15 shows two procedures to accomplish the test. The method chosen was procedure A, which is designed mainly for materials that break at comparatively small deflections. Therefore, it was adopted a three-point bending test which the strength is applied at the center of the material and supported in two parallel holders. Furthermore, according to the standard, the radii of the supports and the loading nose must be 5.0 ± 0.1 mm and the crosshead speed should be no higher than 2 mm/min.

To manufacture the specimen according to the standard, the span of the supports and the thickness should be 16:1, and the thickness should not exceed the width of the specimen. Hence, the sample length chosen was 100 mm, the dimension of the span, width and thickness, are respectively 80, 20 e 5 mm. In favor to get the best results in this test, five samples of each percentage were tested.

The stress-strain curve was obtained by plotting the stress for the respective strain at the same time. The data to calculate the stress were given by the universal testing machine. Furthermore, the software Gom Correlate was used in order to extract the true deflection of the specimen by image correlation, in order to calculate the strain.

2.3 Flammability Test

The method for measuring the comparative burning characteristics of solid plastics in a vertical position from ASTM D3801-10 was performed to characterize PUF flammability properties. The obtained results are intended to serve as initial indication of their approval for use in determined applications.

For this method, the flame-impingement time is 10 ± 0.5 s, after which the flame is moved away from the specimen, sufficiently so that there is no effect on the burning PUF, and the after-flame time (t1) is measured, in seconds. When the flame on the specimen ceases, the burner should be immediately placed under it again, maintaining the flame during 10 ± 0.5 s and then measuring the second after-flame time (t2) and after-glow (t3), in seconds.

Table 2, adapted from ASTM D3801-10 standard Appendix, shows the categories in which the specimens behavior shall be classified, using the gotten results to properly assign the PUF samples to the classes.

Table 2. Materials flammability classifications for vertical burning test method

Criteria Conditions	V0	V1	V2
After-flame time for each individual specimen, t_1 or t_2	≤10 s	≤30 s	≤30 s
Total after-flame time (t_1 plus t_2 for the five specimens)	≤50 s	≤250 s	≤250 s
After-flame or after-glow of any specimen up to the holding clamp	No	No	No
Cotton indicator ignited by flaming particles or drops	No	No	Yes

The classifications listed above define the flammability characteristics of the material, ensuring that the material will fit certain applications based in the tested results.

3. RESULTS AND DISCUSSION

As mentioned before, the ideal density differs from the real density once some material remains in the beaker after the homogenization. Table 3 presents the real density measured after molding.

Table 3. Real material densities

ATH added (%)	Expected Density (kg/m³)	Real Density (kg/m³)	Polymer Density (kg/m³)
0	220	179.3	179.3
10	242	199.9	181.7
20	264	206.9	172.4
30	286	225.6	173.5

As shown in Table 3, the mass lost was about 20%, and the polymer density, which discounts the ATH mass, were similar among the samples. The ideal would be polymer densities with the very same values.

3.1 Flexural Test Results

With the acquired images of the flexural test, it was possible to make an image correlation with the software Gom Correlate. The software accomplishes an analysis of the images comparing the sample deflection during the test as shown in the Figure 1. In this way, it would be able to specify the maximum strain before the fracture.

Figure 1. PUF+30% ATH deflection at certain point found with the software Gom Correlate.

The PUF with different quantities of ATH flexural stress-strain curves were plotted with the average results for stress and strain obtained by following the standard ASTM D790-15[E2] and these curves can be seen in the Figure 2.
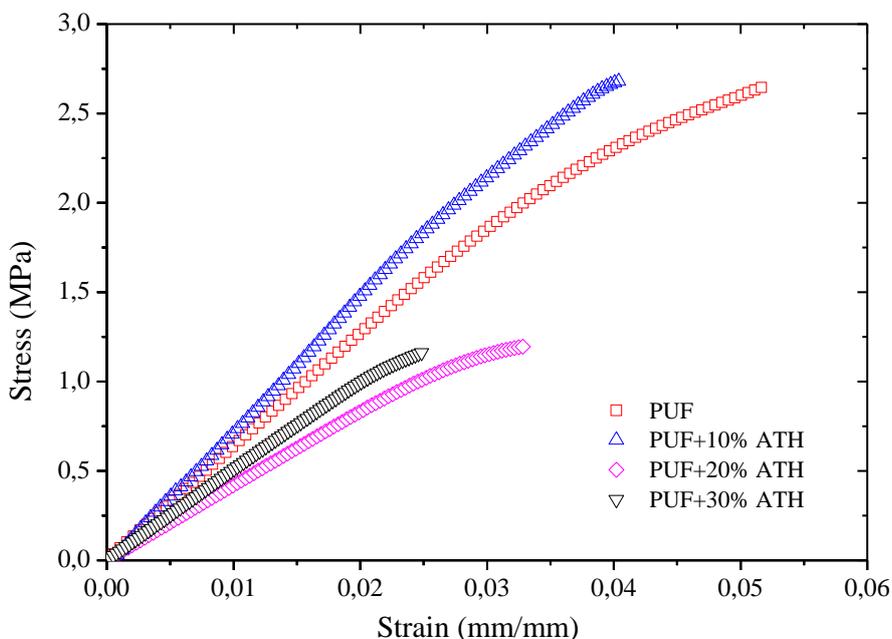

Figure 2. PUF flexural stress-strain curves for each proportion of ATH added

The polyurethane foam average flexural strength (σ_{fm}) and mean maximum flexural strain (ε_{fm}) had different behaviors with different proportions of ATH being added, the exact values for each proportion are better shown in Table 4.

Table 4. Stress-strain average data.

ATH added (%)	σ_{fm} (Mpa)	E (Mpa)	ε_{fm} (mm/mm)
0	2.646	64.085	0.052
10	2.68	72.446	0.04
20	1.196	42.1	0.033
30	1.162	50.549	0.025

Aiming a better interpretation of the values, the use of the standard deviation analysis was adopted. The 5 samples used on each tested ATH proportion showed similar results among each other, presenting acceptable standard deviations. The mean values in Table 4 with the respective standard deviations are shown in the Figure 3.
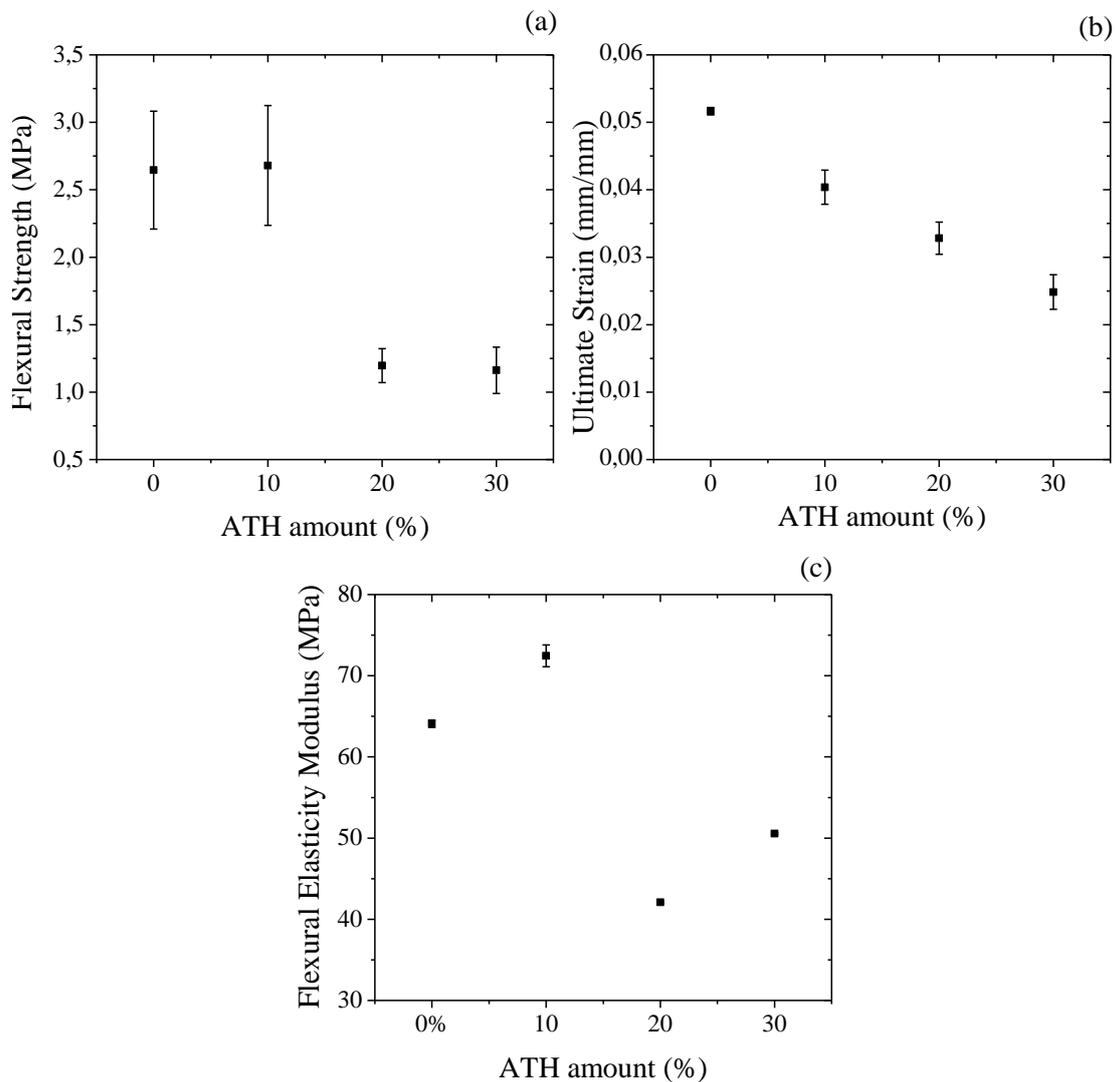

Figure 3. Mean flexural strength (a), Mean ultimate strain (b), and mean flexural elasticity modulus (c) for each percentage with the respective standard deviation.

As it can be seen from figure 3, the σ_{fm} values for pure PUF and PUF+10% ATH can be considered the same, once their error bars cover both of the mean values, so it is possible to affirm that the addition of 10% ATH did not change the flexural strength of the pure polymer. However, the mixture PUF+20% ATH and PUF+30% ATH presented lower σ_{fm} values than the pure PUF. Furthermore, the values for the both mixtures are similar to each other, and the PUF+20% ATH and PUF+30% ATH standard deviation values allow the assumption of a practically unchanged flexural strength value between these mixtures.

The perceived flexural strain exhibited a practically linear decrement behavior when more ATH was added into the mixture. The PUF+30%ATH mixture showed a 50% smaller value than the pure polymeric foam. The flexural strain standard deviation values were satisfactory and presented no significant changes in the data analysis.

The elasticity modulus showed an almost insignificant sample standard deviation. However, it presented an unexpected behavior. The addition of 10% ATH into the pure PUF showed a higher stiffness than the pure polymer, although, the mixture PUF+20%ATH presented the smallest elasticity modulus among the tested foams, moreover, the 30% ATH doped PUF exhibited a rather higher value.

3.2 Flammability Test Results

Table 5 shows the obtained results from the vertical flammability test method, in which PUF added with different concentrations of ATH were tested, so it could be possible to compare the influence exerted to the material flammability properties by increasing the flame-retardant level in the mixture.

Table 5. Vertical burning test results

Samples	t_1 (s)	t_2 (s)	Total after-flame (s)
PUF	3,55	2,11	112,46[2]
	24,34	-[1]	
	27,57	-[1]	
	4,68	25,97	
	24,24	-[1]	
PUF + 10% ATH	2,22	30,42	125,64
	2,67	20,51	
	1,72	9,31	
	1,51	29,60	
	2,53	25,15	
PUF + 20% ATH	5,11	29,72	88,49
	2,60	1,60	
	2,05	41,00	
	1,87	1,11	
	2,36	1,07	
PUF + 30% ATH	7,70	28,06	51,51
	1,45	1,35	
	1,89	1,39	
	2,92	3,58	
	1,50	1,67	

[1]The excess of particle drops inside the Bunsen burner harmed the timekeeping.
[2]This value should be neglected once the test could not follow the standard.

It was expected that the flame retardancy of PUFs would be improved with increased levels of ATH. This characteristic was proven by the total after-flame values, that decreased as the concentration of flame-retardant in the set of specimens was higher.

Figure 4 shows the specimens condition after being performed the flammability test, with specimens supported in vertical position.

Figure 4. PUF specimens after flammability test in vertical position.

In accordance to ASTM D3801-10 classification system, that comparatively determines the burning characteristics of solid plastics in vertical position, the analysis was made. As explained in Table 2, if any specimen burns up to the clamp, the material cannot be assigned to the available categories. As shows Figure 4, the flame-front passes the clamp for specimens doped with plus 10%, 20% and 30% in mass of ATH. Even with a good performance in the vertical burning test, the PUF+30%ATH could not be classified as V2 because of some completely burned samples.

4. CONCLUSIONS

Considering the results of this study, the pure PUF presented very different mechanical behavior than the doped PUF in different proportions. Also, the comparison of the 4 different mixtures exhibited a linear ultimate flexural strain decrement when more ATH was added into the mixture. As Figure 3 shows, the more addition of ATH showed different flexural strength and elasticity modulus performances. The σ_{fm} values for 0% (2.646 MPa) and 10% (2.68 MPa) were similar. Even with the σ_{fm} numbers for 20% (1.196 MPa) and 30% (1.162 MPa) being similar between each other, the comparison with smaller percentages of added ATH shows a non-linear σ_{fm} performance. This changeable behavior was unexpected and it may be explained by the complexity of the flexural test, which the specimen is submitted to compression and tensile stresses, since the addition of ATH enhances the compression properties and decreases the tensile strength characteristics acting as a stress concentrator. Also, this behavior could be explained by the polymer density differences arisen from the manufacturing process.

The flammability results of this paper presented a higher flame retardancy ratio when comparing the pure polyurethane foam to the ATH doped PUF. The ATH doping process showed a progressive flame retardancy as its proportion increased. The pure PUF total after-flame number could not be analyzed because of the massive particle drops amount, which indicates the voracious flammability of the pure polymer. The 4 criteria were used in order to classify the mixtures. The total after-flame number criterion had positive responses and the 3 tested doped PUF would be easily classified as V1. However, the individual t1 and t2 criterion numbers showed unacceptable values for the mixtures PUF+10%ATH and PUF+10%ATH, these mixtures presented individual burning times higher than the necessary number to classify the material (30 s), although, the mixture PUF+30%ATH passed this test and could be classified as V1 following this criterion. As for the cotton indicator criterion, none of the materials passed the test, presenting incendiary particle drops, so it reduced the minimum mixtures classification for V2. Finally, for the after-flame or after-glow of any specimen up to the holding clamp criterion, none of the tested materials passed because all of them presented at least one sample with flame up to the holding clamp, making the materials unable to be classified. Furthermore, the results for the flammability tests were good and an improvement can be easily seen. However, the numbers were not good enough to classify the materials as V2 (the worst flammability classification presented).

The main idea of this paper was to show the flammability properties enhancements that the green polyurethane foam could have when doped with alumina trihydrate and compare the mechanical characteristics results with different mixtures percentages, thereby increasing the application range for a non petro-based polymeric foam.

5. ACKNOWLEDGEMENTS

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