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Thermal Stability and Flammability Properties of Filled Rigid Polyurethane/ Aluminium Hydroxide Composite Foam

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Rigid polyurethane foam (RPUF) has been prepared at various amounts of aluminium hydroxide (ATH) flame retardants (10,20,30,40,50 wt. %). This study aims to examine the thermal, and fire behaviour of RPUF by exploring the ATH as a flame retardant. The effect of different contents of ATH constituents on RPUF was investigated. Results from thermogravimetric analysis TGA showed that the thermal stabilities of composite foam were higher than that of pure RPUF. The results of the limiting oxygen index test showed that 50 wt. % aluminium hydroxide (ATH) enhanced the limiting oxygen index (LOI) value of the composite by 23 % compared to pure RPUF. All aluminium hydroxide (ATH) contents were observed to have contributed to the boosted flame retardancy of RPUF. The RPUF composite showed great potential for being employed as insulation material.

1. Introduction

Polymeric foams consist of both solid and gaseous phases. They are classified into two categories: thermoplastics and thermosetting foams (Lee and Ramesh et al., 2004). They can be rigid, flexible foam, or elastomeric and are produced from a wide range of polymers such as polyurethane (PU). Foam production worldwide has been dominated by polyurethane foams (PUFs), followed by polystyrene and polyvinyl chloride foams (Titow, 2001). Polyurethane (PU) faces limitations in structural, electronic, and transportation applications due to ignition, high flammability, and limited thermal stability. Additionally, its low dimensional stability poses challenges in insulation applications (Liu et al., 2016; Srihanum et al., 2022). Rigid polyurethane foam (RPUF) is categorized as a flammable polymer, releasing substantial heat and toxic gases like carbon monoxide and hydrogen cyanide during a fire outbreak (Chen et al., 2018). This has necessitated the incorporation of flame retardants (FR) in these sectors. PU's primary market is in PU foam, which encompasses various foaming systems. Rigid polyurethane foam (RPUF) is a polymer-based foam featuring carbamate groups in its main chain. Consequently, in the event of a fire, rigid polyurethane foam (RPUF) undergoes rapid combustion, with the flames spreading quickly due to its porous structure, low thermal inertia, and extensive surface area. Inhaling these emitted gases presents a significant health risk to humans during combustion (Zhou et al., 2020). Therefore, it is essential to enhance the fire retardancy and smoke-suppressing characteristics of rigid polyurethane foam (RPUF) by incorporating flame retardants (FR) (Cao et al., 2017). Like other PU foams, rigid polyurethane foam properties can be easily modified by incorporating inorganic hydroxide fillers into the polymer to produce a composite with superior flammability and thermal performance (Peng et al., 2019; Sałasińska et al., 2021). Commonly employed inorganic hydroxide fillers, such as magnesium hydroxide, aluminium hydroxide (ATH), and layered double hydroxides, are recognized for their non-toxic and environmentally friendly attributes. They are routinely integrated into polymer matrices to augment thermal and flammability properties (Pang et al., 2019). Among these, aluminium hydroxide (ATH), stands out due to its cost-effectiveness, lack of odor, ease of handling, non-toxicity, chemical inertness, and non-volatility. In applications where aluminium hydroxide (ATH) filled composites are subjected to heat and subsequent combustion, aluminium hydroxide (ATH), serves to absorb and uniformly disperse the applied heat within its particles, thereby mitigating the heating rate of the composite (Modesti et al., 2002). The effective dispersion of fillers within the matrix significantly influences the reinforcing impact.

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Therefore, this study's goals are to investigate and compare the influence of pure rigid polyurethane foam (RPUF) and different content of aluminium hydroxide (ATH) filler on the thermal, and flammability properties of rigid PU foam-based composites.

2. Experimental

2.1 materials

Polyol (Component A) is one of the materials used to produce rigid PU foam, it is a liquid mixture that contains polyester polyol, flameproofing agent, benzyl-dimethylamine content 1 % as a catalyst, 1,1-dichloro-1-fluroethane content 20 % as blowing agent, and N, N, N', N' – tetramethyl hexamethylenediamine content 0.1 % as crosslinker. In contrast, isocyanate (Component B) was diphenylmethane-4,4 diisocyanate (PMDI). Wee Tee Tong Chemicals Pte Ltd., Malaysia, supplied both ready mixed components A and B. Aluminium hydroxide (ATH) was purchased from Merck Malaysia Sdn.Bhd. All materials were utilized without any additional processing.

2.2 Preparation of rigid PU Foam Composite

The rigid polyurethane foam (RPUF) was synthesized via a one-step mixing procedure utilizing components A and B, as outlined in Table 1. Initially, component A (polyol) underwent stirring with a high-speed mechanical stirrer and underwent a 2-minute degassing period. Subsequently, the flame retardant was introduced into a beaker containing the polyol. The resulting pre-mixture was stirred at 1000 rpm for two minutes using a mechanical stirrer to achieve a homogeneous solution. Once the flame retardant was thoroughly wetted and dispersed within the mixture, component B (diisocyanate) was added to the pre-mixture solution, undergoing continuous stirring for a brief duration. The resulting mixture was then transferred into a close-type stainless-steel mould to facilitate creaming and self-rising. Following this, the mould was left at room temperature for 24 hours before being cut into specimens to ensure complete curing.

Table 1: Formulation of rigid PU foams with different content of aluminium hydroxide (ATH) ATH used in this study.

Samples	Polyol	PMDI	ATH wt. %
Pure RPUF	50	50	0
RPUF/ATH	50	50	10
RPUF/ATH	50	50	20
RPUF/ATH	50	50	30
RPUF/ATH	50	50	40
RPUF/ATH	50	50	50

2.3 Characterization of RPUF/ATH

2.3.1 Thermal properties of RPUF/ATH

Thermal gravimetric analysis (TGA) was performed using (TGA Q500 V20.13 build 39) instrument to investigate the thermal degradation of the RPUF/ATH composite. The weight changes of the sample were monitored with respect to temperature. The sample was placed in a platinum pan and subjected to heating from 28 °C to 700 °C at a rate of 10 °C/min, within a nitrogen gas atmosphere flowing at 100 mL/min.

2.3.2 Limiting Oxygen Index (LOI) test

The limiting oxygen index (LOI) test was conducted following the ASTM D2863-97 standard, The analysis involved preparing five samples from each formulation, each with dimensions of 100 × 12.5 × 12.5 mm³ (length, width, and thickness). The limiting oxygen index (LOI) values were recorded by burning five samples for each formulation. According to Alongi et al. (2015), polymers with limiting oxygen index (LOI) values above 27 % are considered self-quenching, those below 21 % are highly combustible in the air, and those falling between 21-27 % are classified as slow-burning.

3. Results and discussion

3.1 Thermal Gravimetric Analysis (TGA) of RPUF/ATH Composites

As shown in Figure 1 (TGA Curve) T_5 (the beginning of degradation) for pure rigid polyurethane foam (RPUF) of 231 °C was recorded. All the samples produced major two-stage thermal degradation. Release of volatile molecules namely water molecules was detected due to the high moisture uptake of the porous RPUF below 250 °C. The initial stage of the breakdown of rigid polyurethane foam (RPUF) arose around 231- 424 °C, attributed to the break in urethane linkages. The second stage occurred at about 512-712 ^{o}C, ascribed to the cleavage of strong bonds like aromatic groups, aliphatic carbon-carbon, and flame retardants (Kairytė et al., 2020). The RPUF/ATH composites at the highest content of aluminium hydroxide (ATH) 50 wt. % displayed a major peak at approximately 316 ^{o}C, mainly ascribed to the superior heat absorbing capabilities of aluminium hydroxide (ATH) at higher loading, resulting in increased degradation temperature (Akdogan et al., 2020). While T_{max} for pure rigid polyurethane foam (RPUF) was observed to be 296 ^{o}C, there was a considerable increase in T_{max} for modified rigid polyurethane foam (RPUF), ranging from 304-316 ^{o}C, increasing with an increase in aluminium hydroxide (ATH) content. This can be interpreted as an enhancement in thermal stability after adding aluminium hydroxide (ATH). These increases could be credited to the water molecules released from aluminium hydroxide (ATH); the water molecules tend to cool the hot polymer hence the treated rigid foam requires higher heat energy to break down ((Thirumal, M et al., 2010). Polymer's degradation temperature ought to rise generally as aluminium hydroxide (ATH) content increases. That's because aluminium hydroxide (ATH) undergoes endothermic breakdown, lowering the temperature in the area around the components. Also, the combustible gases are reduced by water dilution and the development of a protective layer of aluminium oxide, which serves as a barrier for the passage of oxygen and fuel into polymers. On the other hand, Figure 1 (DTG curve) shows the DTG curve for pure rigid polyurethane foam and ATH-modified rigid polyurethane foam at different loading. As observed, rigid polyurethane foam/aluminium hydroxide (RPUF/ATH) composites displayed a shoulder peak; this may be because of the removal of surface-active complexes used in ATH to enhance its dispersal in the polymer matrix. The DTG curves indicate that the thermal stabilities of rigid polyurethane foam/aluminium hydroxide (RPUF/ATH) composites are higher compared to pure rigid polyurethane foam (RPUF). The unfilled foam thermally breaks down with a greater decomposition rate than the filled foam. This can be associated with the formation of different thermally stable constituents namely phosphorous-based compounds and aluminium oxide during the degradation. The aluminium hydroxide (ATH) as a flame retardant in rigid polyurethane foam (RPUF) has huge capacities to form a compact char hence shielding the inner bulk materials. Shown in Table 2 are the char residue values of the filled and unfilled rigid polyurethane foam composites. The weight residue reveals that the highest volume of ash was recorded with (50 wt. %) ATH loading. More so, the mass residual of RPUF/ATH (50 wt. %) and RPUF/ATH (40 wt. %) were 29.16 and 25.85 wt. %. These findings demonstrate that the aluminium hydroxide (ATH) boosted the thermal stability of the composite by reducing weight loss, moving it to a higher decomposition temperature, and significantly increasing the remaining char concentration compared to pure rigid polyurethane foam (RPUF).

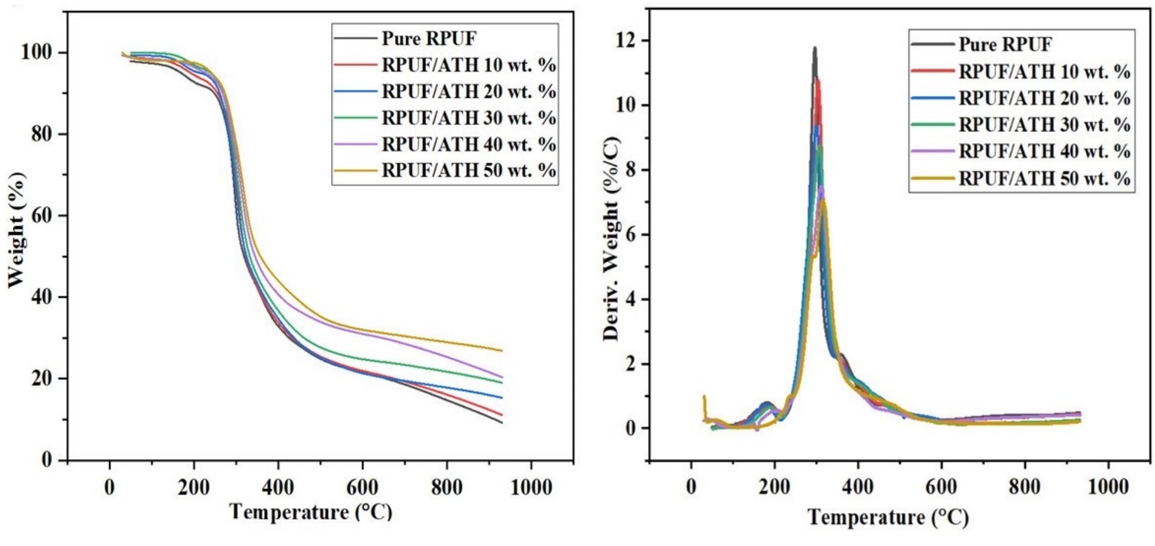

Figure 1: TGA and DTG curves of RPUF and RPUF/ATH composites incorporated with 10-50 wt. % ATH.

Table 2: Thermogravimetric data for pure RPUF and RPUF/ATH composites

Samples	T_5 (°C)	T_{50} (°C)	T_{max} (°C)	Char residue (%) at 600 °C
Pure RPUF	231	318	296	15.18
RPUF/ATH10 wt.%	252	326	304	16.42
RPUF/ATH20 wt. %	256	333	300	18.01
RPUF/ATH30 wt. %	278	334	306	21.20
RPUF/ATH40 wt. %	266	346	314	25.85
RPUF/ATH50 wt. %	280	360	316	29.16

3.2 Limiting Oxygen Index (LOI)

Table 3 depicts the limiting oxygen index (LOI) values for the aluminium hydroxide (ATH) incorporated composites blending. According to the specimen observation, all the composites containing aluminium hydroxide (ATH) show higher limiting oxygen index (LOI) values as the aluminium hydroxide (ATH) loading increases compared with pristine rigid polyurethane foam (RPUF). But RPUF/ATH (50 wt. %) have the best improved limiting oxygen index (LOI) of 23 %. Comparing the limiting oxygen index (LOI) of three composites, RPUF/ATH (20 wt. %), RPUF/ATH (30 wt. %), and RPUF/ATH (40 wt. %), present a relative increase in their limiting oxygen index (LOI). These outcomes suggest they are combustion-resistant with slow-burning attributes. It was documented in a previous study that composites with a limiting oxygen index (LOI) range of 21-27 % are classed as slow-burning. The major reason responsible for the increase in RPUF/ATH composite limiting oxygen index (LOI) aluminium hydroxide (ATH) is an organic filler with crystal water in its chemical structure. Hence, during the endothermic reaction at (220 °C – 450 °C) it releases about 34 wt.% steam. This lowers the composite temperature during combustion and the released steam dilutes the combustible gases, resulting in increased limiting oxygen index (LOI). Additionally, aluminium hydroxide (ATH) exhibits a dehydration reaction to generate Al_2O_3 and carbonize the composites giving rise to flammable volatiles and preventing the spread of flame (Zhu et al., 2014). Some previous studies have reported improved limiting oxygen index (LOI) values when some amount of aluminium hydroxide (ATH) flame retardant additives were incorporated into a polymer matrix such as polyurethane foam filled with a mixture of aluminium hydroxide and triphenyl phosphate (PUF/ATH/TPP) (Thirumal et al., 2008). The presence of aluminium hydroxide (ATH) in the composites contributed to the reduction in flame-spread rate and increased limiting oxygen index (LOI). Similarly, aluminium hydroxide (ATH) played a synergistic role in the rigid polyurethane foam/aluminium hydroxide/Dimethyl methyl phosphonate (RPUF/ATH/DMMP) hybrid composite by substantially enhancing the composite flame retardancy (Zhu et al., 2022). Like another additive-type flame retardant (such as magnesium hydroxide), aluminium hydroxide (ATH) retard polymer heat capacity, its high volume when present in the composite function as a solid phase diluter, and their addition into any resins, rubber, and plastics can reduce the concentration of flammable substances in composite materials (Ahmad Ramazani et al., 2008; Peng et al., 2019).

Table 3: Limiting Oxygen Index (LOI) of pristine RPUF and RPUF/ATH composites.

Samples	ATH Loading	LOI
S1	0	18
S2	10	19
S3	20	20
S4	30	21
S5	40	22
S6	50	23

*S1 stands for sample 1

As illustrated in Figure 2, (a) is the limiting oxygen index (LOI) residue of pristine rigid foam, (b-f) for rigid polyurethane foam/aluminium hydroxide (RPUF/ATH) (10-50 wt. %) respectively. From the digital pictures, it was established that pristine rigid polyurethane foam (RPUF) char residue is small and light. Within a short period, this sample burns profusely, leaving behind a small residue insufficient to protect underneath the polymer. An indication of their poor flame resistance on exposure. However, RPUF/ATH 30 wt. % and RPUF/ATH 40 wt. % had bulkier char residue, an indication of superior fire resistance compared to pristine rigid polyurethane foam (RPUF). A recent study reported that the amount and quality of char are responsible for excess non-flammable residues, acting as a physical shield and enhancing composite fire retardancy efficiency (Xiao et al., 2021). For RPUF/ATH 50 wt. %, the higher concentration of aluminium hydroxide (ATH) in the composite was responsible for their higher limiting oxygen index (LOI) value. Aluminium hydroxide (ATH) clogs the entire surface of the rigid foam thereby disrupting any flame propagation hence no major burning took place.

The presence of 50 phr aluminium hydroxide (ATH) in rigid polyisocyanurate-PU foam composite substantially boosted their resistance to flame during combustion and the marginal burning residue was noticed.

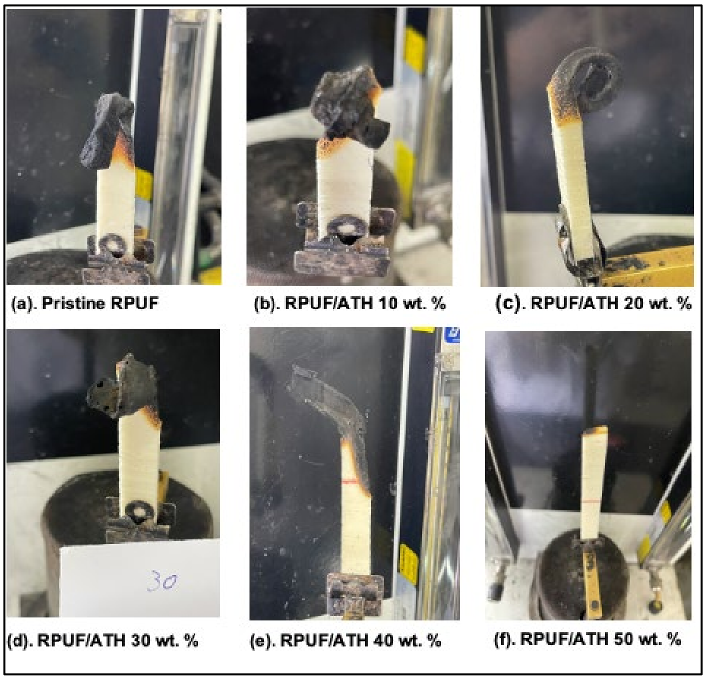

Figure 2: Limiting oxygen index (LOI) test residue images of RPUF composites at (a) 0 wt. % ATH, (b) 10 wt. % ATH, (c) 20 wt. % ATH, (d) 30 wt. % ATH, (e) 50 wt. % ATH.

4. Conclusions

Rigid polyurethane foam (RPUF) composites were satisfactorily prepared and modified with increasing incorporation of 10-50 wt. % ATH as a standalone filler using a step one-shot system. The RPUF/ATH composites were characterized in thermal stability using TGA, and flammability properties via the limiting oxygen index (LOI) test. The measurement of RPUF/ATH thermal stability under a nitrogen gas environment showed that the composites modified with 50 wt. % ATH displayed the highest improvements. The addition of ATH also confers superior heat-absorbing capacities and higher degradation temperature on the composites. While burning, ATH releases water molecules that cool the molten polymer, resulting in a lower temperature around the composites. Both ATH 50 wt. % and ATH 40 wt. % modified composites showed the highest char residue, a confirmation of the improved thermal stability of the composites. Data obtained from the limiting oxygen index (LOI) test confirmed a boost in the fire retardancy of RPUF/ATH composite specimens due to the addition of ATHs. The limiting oxygen index (LOI) was greatly improved and excellent at 50 wt. % ATH loading. The mechanism by which fire retardancy of RPUF/ATH composites improved is via the creation of an unbroken solid char layer in the condensed phase during the decomposition of the polymer matrix. The char structure efficiently hinders the inside thermal decomposition products into the flame zone and that of the oxygen the underneath polymer matrix. In summary, this study presents a novel technique for the fabrication of filled rigid polyurethane (RPUF) composite foam using aluminium hydroxide (ATH) as a flame retardant. The main contribution of this work lies in the optimization of ATH content, implementation of efficient mixing and dispersion methods, utilization of a mould-based creaming and self-rising process, and a strong emphasis on reproducibility and scalability. By employing this unique approach, this study successfully produces foam samples exhibiting enhanced thermal stability, improved flame retardancy, and significant potential for various applications as insulation materials. The study offers valuable insights into the thermal stability and flammability characteristics of these composites, highlighting their practical utility in industries where fire safety and thermal performance are of utmost importance.

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