

Aluminium Hydroxide/Graphene-reinforced Rigid Polyurethane Foam Hybrid Composites

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ABSTRACT

In this study, rigid polyurethane foams (RPUF) were successfully modified using 30 wt.% aluminium hydroxides (ATH), 1.0 pphp silicone surfactant, and different concentrations of graphene, using a one-shot one-step foaming method. This study aims to improve the compressive strength, flame retardancy, and thermal properties of RPUF by creating a synergistic effect between ATH and graphene in fire-retardant RPUF hybrid composites. The effects of a fixed amount of ATH and silicone surfactant and various loadings of graphene on RPUF were investigated. The results show that 0.5 wt.% graphene loading confers the best compression performance on the hybrid composite. Their compressive strength value of 12.58 KPa was higher than virgin RPUF (4.07 KPa) and RPUF/ATH (9.89 KPa). FTIR confirmed the functional groups in the virgin RPUF but could not identify new functional groups in most modified composites. The smallest amount of graphene addition (0.5 wt.%) produced a more stable hybrid composite structure. At 3.0 wt.% graphene addition,

the maximum decomposition temperature of the RPUF/ATH hybrid composite was recorded (539°C), which was enhanced by 50% compared to virgin RPUF (296°C), and the highest char residue of 17.46% was observed. The incorporation of graphene enhanced the thermal firmness of the hybrid composite. The study also revealed an enhancement in the fire resistance of the hybrid composite. The LOI and UL-94 results showed that incorporating 3.0 wt.%

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enables increased LOI value and V-0 classification compared to virgin samples. This hybrid composite can be used in high-performance building insulation applications.

Keywords: Aluminium hydroxides (ATH), fire behaviour, flammability, graphene, hybrid flame retardant, rigid polyurethane foam

INTRODUCTION

Owing to their durability and versatility, polyurethanes (PU) are in high demand in the fields of construction, automobiles, and refrigeration for thermal insulation (Dhaliwal et al., 2020; Kavšek et al., 2022; Liu & Hu, 2020). Polyurethane foam is the most common application of PUs in the central consumer segment (Shoaib et al., 2014). According to studies by Eaves (2004) and Titow (2001), polyurethane (PU) still accounts for 67% of the global foam market, ahead of polyvinyl chloride (PVC) and polystyrene (PS) (Muhammed et al., 2023). PU foam is divided into rigid and flexible categories based on its intended use. Each category differs in the functionality and polyol type used for synthesis (Baguian et al., 2021; Shoaib et al., 2014).

Among the listed categories, rigid polyurethane foam (RPUF) has been more widely studied because of its superior application ranges in transportation (Tiuc et al., 2019), sealants (Eling et al., 2020), insulation materials (Srihanum et al., 2022; Tiuc et al., 2022), packaging (Jonjaroen et al., 2020), and construction (Ju et al., 2020; Lorusso et al., 2017), among others. RPUF is used as a structural material owing to its lightweight, excellent strength-to-weight ratio, and capacity to absorb energy (Alis et al., 2019; Kumar & Kaur, 2017). RPUFs are produced with a higher isocyanate (NCO) content, which increases the hard segment composition of the system. They are highly crosslinked three-dimensional polymers with closed-cell structures, low thermal conductivities, high compression strengths, and low densities. These attributes are attributed to their high porosity, strength-to-weight ratio, and low moisture permeability (Chen et al., 2014; Kerche et al., 2020). Similar to other PU foams, the properties of RPUF can be easily modified by incorporating inorganic hydroxide fillers and nanoparticles into the polymer matrix to produce composites with superior mechanical and thermal performance (Mohamad et al., 2021; Peng et al., 2019; Sałasińska et al., 2021).

Traditional inorganic hydroxide fillers, such as magnesium hydroxide, aluminium hydroxide (ATH), and layered double hydroxides, are non-toxic and ecologically friendly. They are commonly used as reinforcing materials in a polymer matrix to enhance their mechanical, thermal, and flammability properties (Pang et al., 2019; Rocha et al., 2021; Wang et al., 2017). ATH, in particular, is a popular choice owing to its chemical inertness, ease of handling, odourless, low cost, and non-volatility. When composites filled with ATH are heated and burned, they absorb heat. It leads to a uniform distribution of absorbed heat within the ATH particles, thereby reducing the heating rate of the composite (Cheng et

al., 2014; Modesti et al., 2002). On the other hand, nanoparticle fillers like graphene are used in smaller quantities compared to traditional particles, which has little impact on the PU foaming process. The dispersion of the filler in the matrix played a significant role in the reinforcement effect. Graphene is well-known for its excellent mechanical properties, including a fracture strength of 125 GPa, high Young's modulus of 1.1 TPa (Lee et al., 2008), and an ideal specific surface area of 2630 m²/g (Stoller et al., 2008).

Despite its unique properties, RPUF has significant limitations, including ease of ignition, high flammability, low mechanical strength, and low thermal stability. Additionally, their low dimensional stability creates problems in insulation (Liu et al., 2016; Srihanum et al., 2022). RPUF is a flammable polymer. In a fire outbreak, foams release a large amount of heat and toxic gases such as carbon monoxide and hydrogen cyanide (Chen et al., 2018). Previous studies have shown that incorporating more than one type of flame retardant (FR) (such as organic and inorganic FR) into polymer foam can significantly enhance the mechanical, thermal, and flammability properties of foam composites (Feng et al., 2016; Huang et al., 2020). Członka et al. (2021) reported the effect of montmorillonite (MMT)-modified sage filler on the mechanical and thermal properties of RPUF composites. The results showed that modifying salvia (SO) filler with MMT improved the interphase compatibility between the filler surface and PUR matrix. This modification also results in RPUF composites with improved compressive strength, thermal stability, and flame retardancy.

Wang et al. (2018) used magnesium hydroxide (MH) nanosheets to create core-shell expandable graphite (EG) flame-retardant fragments using a hetero-coagulation technique. Thus, the storage modulus and cell structure of RPUF-EG@MH were enhanced. The MH nanosheet shell successfully increased the foam's limiting oxygen index (LOI), and the interface adhesion between the expandable graphite (EG) and the matrix was improved. Pen et al. (2019) compared the effects of MH and ATH on the combustion resistance, compressive stress, and cell structure of RPUF. They found that ATH performed better than MH-modified RPUF composites because the RPUF/ATH composite had larger cells, higher maximum compressive stress, and an optimal LOI value. Various studies have compared the effects of graphene and its derivatives on the properties of polymer foam composites. In a recent survey by Thiyagu et al. (2021), different amounts of graphene were incorporated into polyurethane foam, and the thermal stability and morphology of the composites were investigated. The SEM results confirmed that graphene was evenly dispersed in the PU matrix, and its incorporation increased the thermal stability of the foam composites. Based on the results of Yao et al. (2020), the addition of flexible graphene sheets enhanced the flexibility, fire behaviour, and thermal degradation temperature of PU composites.

Several studies have been conducted on the influence of dual fillers and nanofillers on the preparation and properties of rigid polyurethane foams. Sałasińska et al. (2021) developed a

dual non-halogen flame retardants (FRs) system using graphene-oxide (GO) and histidine for rigid PU foam to reduce smoke emissions and enhance its fire retardancy. Liu et al. (2021) examined the impact of different concentrations of GO-hollow glass microspheres on the morphology, density, and compressive properties of RPUF. Liu et al. (2020) summarised the improvements in the thermal stability and fire safety of RPUF attributed to the synergistic relationship between expandable graphite and phosphorus/nitrogen compounds. A summary of previous studies on the flame-retardant behaviour of RPUF is presented in Table 1.

This study aims to address the existing research gap by investigating and comparing the morphology, compressive strength, and thermal and flammability properties of a hybrid composite system utilising aluminium hydroxide (ATH) and graphene as reinforcing fillers in rigid polyurethane foam (RPUF). To the best of our knowledge, no previous studies have explored the performance of hybrid ATH/graphene fillers in RPUF composite systems, specifically in terms of their morphology, compressive strength, flammability, and thermal properties. In addition, we incorporated a silicone surfactant into the RPUF formulation to control the cell size of the rigid foam and reduce its surface tension. Therefore, this

Table 1

Summarises past and recent literature on the flame-retardant behaviour of RPUF

Paper Title/Focus	Contribution	Reference
Fire behaviour of PU foam with non-halogen fire retardants (histidine/modified graphene oxide) system	The authors obtained a reduction in the total heat release rate, heat release rate, maximum average rate of heat emission, total heat release (THR) and total smoke release for modified RPUF.	Sařasińska et al., 2021
Preparation and evaluation of RPUF flame retardant (functionalised graphene oxide)	3 wt.% functionalised GO enhanced the flame retardancy of the foam: reduction in peak heat release rate (PHRR) by 25% and total smoke production by 15% compared to pure RPUF.	Zhou et al., 2023
Incorporation of multiple inorganic fillers as viable synergistic agents for enhancing the flame retardancy of intumescent flame retardant (IFR)	RPUF/IFR had a good performance, with a low PHRR of 82.12 kW/m ² , THR of 15.15 MJ/m ² , and a high LOI value of 36% compared to the untreated sample.	Lee et al., 2022
Flammability properties of novel IFR (APP/sepiolite/melamine) in RPUF	The composite's limiting oxygen index (LOI) value increased to 23.20% compared to 17.0% for pure RPUF. The V-0 rating was obtained for RPUF/IFR 16 phr in the UL-94 test. The lowest after-flame time after ignition (21.4 s) was obtained at this formulation compared to other samples.	Mohammad et al., 2021
RPUF was prepared and reinforced by incorporating hydrolysed keratin (HK) to enhance foam smoke suppression and flame retardancy.	The addition of HK improved the LOI and PHRR of the foam, but the THR of the modified foam decreased. The HRR of foam/HK5 was reduced by 28.8 kW/m ² compared with pure foam, and the THR of foam/HK5 is 0.74 MJ/m ² lower than the untreated foam. HK5 wt.% had the most obvious smoke suppression effect	Zhang et al., 2023

study investigates and compares the performance of RPUF-based composites using pure RPUF and ATH/graphene/silicone surfactant hybrid filler systems. This manuscript presents experimental findings regarding the developed composites' structure, morphology, compressive strength, flammability, and thermal properties. The results provide valuable insights into the potential of a hybrid filler system for enhancing the properties of RPUF and contribute to the advancement of materials with improved performance characteristics.

MATERIALS AND METHODS

Materials

This study prepared a flame-retardant rigid polyurethane foam by incorporating a hybrid ATH/graphene. The experiment employed polyol (4500 series), consisting of Part A (with a hydroxyl number of approximately 400–455 mg KOH/g) and Part B. Part A of the formulation has been enhanced with several additional substances, including a catalyst, specifically benzyl-dimethylamine, present at a concentration of 1%. Furthermore, a blowing agent, namely 1,1-dichloro-1-fluoroethane, has been inserted at a concentration of 20%. Finally, a crosslinker, tetramethyl hexamethylenediamine, has been introduced at a concentration of 0.1%. Part B refers to a polymeric diphenylmethane diisocyanate compound, commonly known as P-MDI. Wee Tee Tong Chemicals Pte Ltd., a Malaysia-based company, manufactures Polyol and P-MDI. The foam stabiliser employed in this study was Niax Silicone L-5440, manufactured by Momentive Performance in the United States. Odourless, white, powdered Al (OH)₃ (purchased from Merck KGaA, Germany) and graphene sourced from Soochow Hengqiu Technology were used as flame retardants.

Preparation of Rigid Polyurethane Foam and Composites

Virgin RPUF and ATH/graphene/RPUF foams were prepared in our laboratory using a one-shot, one-stop foaming method. The RPUF and RPUF hybrid composite samples were synthesised in a plastic container. The amounts of ATH and silicone surfactant in the formulations were kept constant at 30 wt.% and 1.0 pphp, respectively, while the graphene content was varied at three different concentrations of 0.5, 2.5, and 3.0 wt.%. First, ATH, graphene, and the silicone surfactant were added to a beaker containing polyol (Part A). The initial mixture was agitated at a rotational speed of 500 revolutions per minute (RPM) for five min using a mechanical stirring device to achieve a uniform and consistent solution. After the flame retardants were completely wetted and dispersed in the mixture, diisocyanate (Part B) was added to the pre-mixed solution with continuous stirring for a few seconds. The ratio of parts A and B was maintained at 1:1. Subsequently, the resulting mixture was poured into a stainless-steel mould to facilitate the creaming and self-rising processes. The modified foams were cured for 24 h at ambient temperature before being cut into samples for analysis. Table 2 shows the formulations of the RPUF and RPUF composites.

Table 2
The formulations of RPUF and hybrid RPUF composites

Sample Code	P-DMI (g)	Polyol (g)	ATH (wt.%)	Graphene (pphp)*
RPUF	50	50	0	0
RPUF/A	50	50	30	0
RPUF/A/GNP	50	50	30	0.5
RPUF/A/GNP	50	50	30	2.5
RPUF/A/GNP	50	50	30	3.0

Note. *(pphp): Parts per hundred polyols in weight

Characterisation of Specimens

The morphological analysis consisted of field emission scanning electron microscopy (FESEM). Field emission scanning electron microscopy (FESEM) was used to examine the spatial arrangement of graphene and aluminium trihydrate (ATH) within a rigid polyurethane (PU) foam. Furthermore, it was necessary to investigate the distribution of closed and open cells within the foam samples to analyse the surface morphology of the samples and examine the foam structure. The SEM used was a Hitachi Japan Tabletop Microscope 3000 model. RPUF/ATH was evaluated using scanning electron microscopy (SEM), and further analysis of the FESEM images was performed using the Zeiss Ks300 imaging system software (3.0 release). Initially, the internal surfaces of the specimens were coated with an auto fine coating to facilitate observation and prevent electrical charge. Subsequently, a thin layer of platinum was applied, and an operating voltage of 2 kilovolts (2 kV) was employed.

For the compressive strength test, the foams were cut to dimensions of $50 \times 50 \times 30$ mm³ (width \times length \times thickness). The test was conducted using a Zwick/Roll Proline Universal Testing Machine from (Ulm, Germany) at room temperature, following the ASTM D 1621-1 standard method. The rise direction of the RPUF was marked, and a crosshead speed rate of 5 mm/min was used. A load cell size was applied until the compressed foam stress reached 10% strain. The strengths of six specimens per sample were measured, and the average of these values was reported.

Fourier Transform Infrared (FTIR) spectroscopy was conducted to determine the presence of specific functional groups in the rigid polyurethane (PU) samples, including urethane linkages and carbonyl groups. The modified samples were also analysed to identify their functional groups. The scanning rate was set from 4000 cm^{-1} to 500 cm^{-1} . A Nicolet iS10 smart modal was used to scan the samples, and the obtained absorption spectra were analysed.

Thermogravimetric analysis (TGA, Q500 V20) was performed to analyse the thermal degradation of the samples. The weight decreases of the samples were measured at different temperatures. Approximately 6.4770 mg of each sample was carefully placed in a platinum

container. The analysis involved subjecting the samples to a temperature range of 28–700°C, with a heating rate of 10°C/min, in the presence of nitrogen gas at a constant flow rate of 100 ml/min. The rate of mass change or weight loss of each sample was carefully measured and recorded throughout the experiment.

The LOI (Limiting Oxygen Index) test was conducted by preparing seven samples for each formulation. Following the specifications outlined in ASTM D2863-97, the minimum burning duration was estimated to be three min. The samples used in the experiment were 100 mm long, 12.5 mm wide, and 12.5 mm thick. The samples were positioned vertically in a clear chimney, and the oxygen and nitrogen flow regulation was carefully controlled. The test was conducted multiple times by varying the oxygen and nitrogen levels to determine the minimal oxygen concentration required for the sample to undergo combustion within three minutes. The LOI of each formulation was assessed by averaging the results of the seven samples.

The flame retardancy of the RPUF/ATH/graphene composites was tested using the Underwriter Laboratories vertical burning test, UL94-V, following the ASTM D 3801-10 standard. The vertical height of the flame during the combustion was 20 mm. Seven samples were prepared for testing, each with dimensions of (130 × 10 × 10) mm³. The samples were then exposed to a flame emitted by the burner for 10 s. The duration for which the flame remained active without external intervention was measured, and the combustion characteristics, including the occurrence of dripping, were carefully monitored. Seven samples for each formulation were tested, and the burning rate was determined using the equation $V = 60 L/t$, where L represents the average length (mm), and t represents the average time (s).

RESULTS AND DISCUSSION

Morphology of RPUF and Hybrid RPUF Composites

Scanning electron microscopy (SEM) was used to analyse the compositions and internal structure of RPUF (Rigid Polyurethane Foam) composites. A hybrid composite system was created by incorporating a 30 wt.% ATH, 1.0 pphp silicone surfactant, and three different concentrations of graphene (0.5, 2.5, and 3.0 wt.%). Figure 1 illustrates the internal structure of the RPUF/ATH composites and the RPUF hybrid composites containing ATH and graphene as hybrid fillers. A surfactant prevents foam collapse by preventing the build-up of gases produced by blowing agents (Baferani et al., 2018). In general, the RPUF hybrid composite exhibited smaller cell sizes than the RPUF/ATH composites, attributed to the nucleation effect of graphene, which produces more bubbles and denser cells. Previous studies have shown that nanoparticles, such as graphene, act as nucleation points, leading to a larger number of cells and, consequently, a smaller cell size (Lorusso et al., 2017).

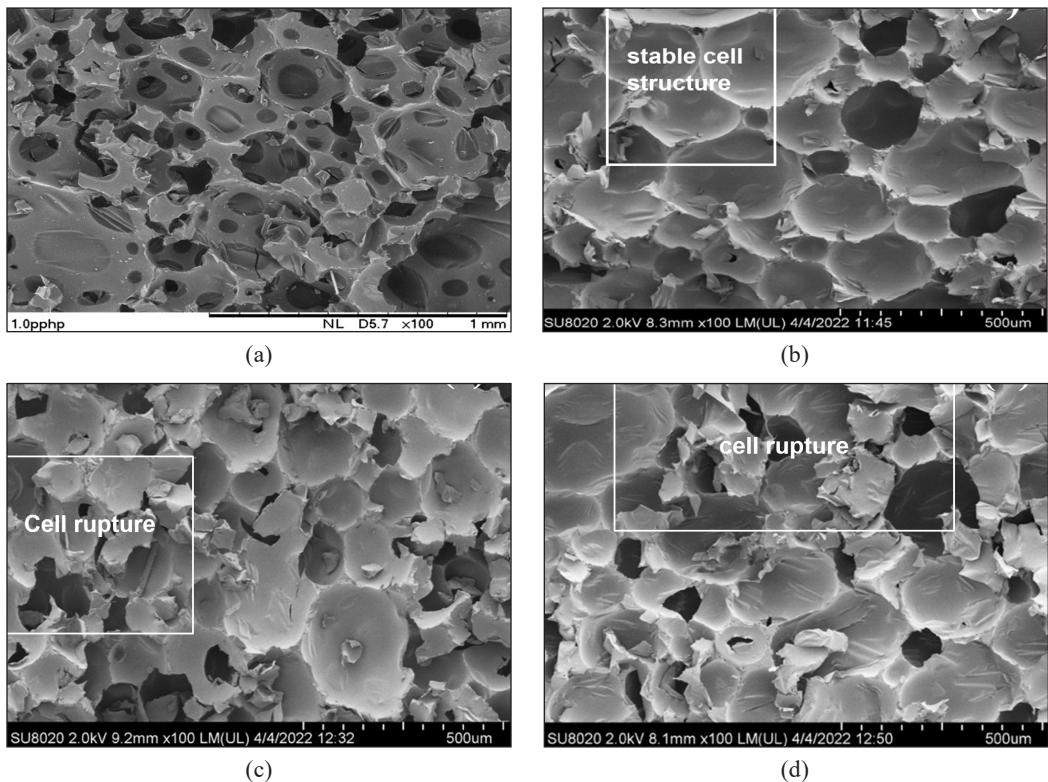


Figure 1. SEM micrographs of RPUF/ATH containing different graphene content: (a) 0 wt.%, (b) 0.5 wt.%, (c) 2.5 wt.%, (d) 3.0 wt.% (Magnification 100 \times).

At a graphene concentration of 0.5 wt.%, the RPUF hybrid composite demonstrates a more stable cell structure with fewer broken cells [Figure 1(b)]. However, as the graphene content was increased to 2.5 wt.% [Figure 1(c)], the internal space becomes compact, and noticeably broken cells are observed. It can be attributed to the presence of graphene, which incorporates rigid particles and hinders the formation and expansion of bubbles during the foaming, leading to further deterioration of the foam structure at higher concentrations (Zhang et al., 2021). Furthermore, an increase in the quantity of graphene resulted in non-uniform cell sizes in the RPUF hybrid composites, as shown in Figures 1(b), 1(c) and 1(d). As the graphene content exceeds 0.5 wt.%, the cell structure collapses rapidly. The research suggests that adding 2.5 to 3.0 wt.% of graphene to RPUF leads to smaller cell growth, but a significant portion of cells collapse, resulting in a disorganised cellular structure. However, the SEM images did not show significant clustering of graphene fillers. This finding is consistent with the observations of other researchers that graphene is beneficial for PU foam. However, excessive concentrations can decrease cell size and create intricate pathways within the foam. Previous studies have attributed the reduction in foam cell size to graphene acting as nucleation points, generating more cells and resulting in a smaller

size. Increasing the graphene content induced rapid changes in the rigid foam structure. While higher concentrations of solid particles, such as graphene, typically reduce cell size and increase cell density, excessive concentrations can decrease and create complex pathways (Chen et al., 2019; Kim et al., 2017; Lorusso et al., 2017).

As observed in other studies, hybrid composites take advantage of the synergies between two fillers in polyurethane systems, enhancing the mechanical and thermal properties (Liu et al., 2021; Pinto et al., 2020). For instance, the SEM result of a multiple FR system (ATH, APP, and others) in RPUF revealed closed-cell structures with adjoining spherical cells, attributed to the strong bond between the flame-retardant system and the PU matrix (Lee et al., 2022). The SEM image of a biobased RPU foam in the presence of ATH shows an elliptical cell shape in two different directions but with the same cross-sectional area (Silva et al., 2022). However, SEM analysis of the RPUF hybrid composites incorporating graphene revealed a smaller cell size, attributed to graphene acting as a nucleation point. However, excessive concentrations of graphene lead to cell collapse and a disorganised cellular structure. Recent studies support these findings and highlight the importance of optimising the graphene concentration to achieve the desired foam and composite properties while avoiding structural deterioration (Jesiak et al., 2023; Yuan et al., 2018). The use of hybrid composites has the potential to further enhance foam properties, and future research can continue to explore the synergistic effects of different fillers on polyurethane systems.

In Figures 2(b), 2(c) and 2(d), the higher magnification images (300×) display the cell morphology of the hybrid composites with varying graphene content. The hexagonal cell shapes in the RPUF hybrid composites are highlighted by red circles in Figure 2. It was observed that when a small amount of graphene filler was added, as depicted in Figure 2(b), the structure of the PU foam cells was improved. This enhancement is characterised by a reduction in the cell diameter, a smoother surface, and a decrease in voids, as shown in Figure 2(b). These improvements can be attributed to the effective dispersion and enhanced bonding between the graphene and RPUF within the hybrid composites. However, as the graphene content increased, as shown in Figures 2(b), 2(c) and 2(d), the uniformity of the cells deteriorated, resulting in rougher surfaces and larger voids. Graphene triggers changes in cell morphology, subsequently affecting the process of cell nucleation (Liu et al., 2021; Shivakumar et al., 2020). Overall, these findings indicate that adding a small amount of graphene filler to the hybrid composites improves the cell structure of the PU foam, leading to enhanced properties, such as reduced cell diameter, smoother surface, and diminished voids. However, an excessive graphene content can have a detrimental effect on cell uniformity, causing rough surfaces and larger voids. Understanding these morphological changes is crucial for optimising the fabrication process and achieving desired material properties in RPUF hybrid composites (Liu et al., 2021; Shivakumar et al., 2020).

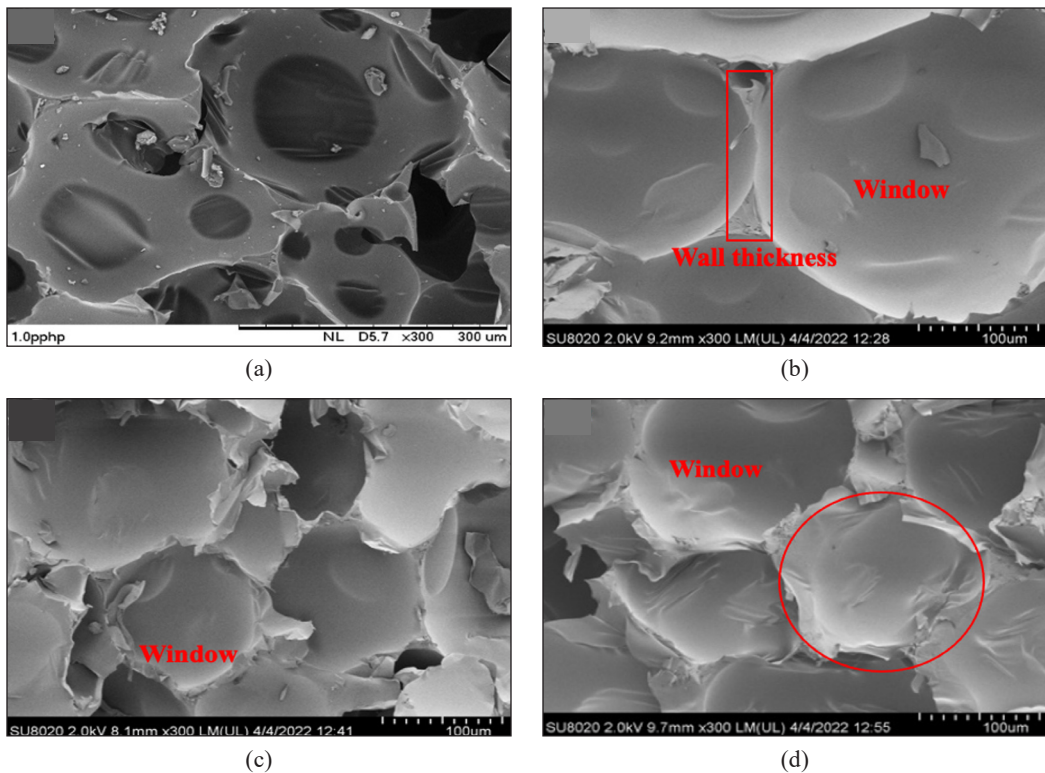


Figure 2. SEM micrographs of RPUF/ATH hybrid composites containing different graphene content: (a) 0 wt.%, (b) 0.5 wt.%, (c) 2.5 wt.%, (d) 3 wt.% (Magnification 300 \times)

Compressive Strength

In industrial applications, dimensional stability is crucial for foams, necessitating high compressive strength. Figure 3 illustrates the mechanical strength of RPUF hybrid composites with varying graphene contents. Among these composites, those containing 0.5 wt.% graphene exhibit the highest compression performance, with an optimal compressive strength of 12.58 KPa. This value surpasses pure RPUF (4.07 KPa) by 67.6% and RPUF/ATH (9.89 KPa) by 21.4%. The addition of graphene-enhanced compressive strength bolsters the durability and hardness of the pore walls, facilitating the formation of dense bubbles within the foam. Similar improvements in mechanical strength were reported by Pinto et al. (2020) and Liu et al. (2021), who introduced graphene and its derivatives as single and hybrid fillers in polyurethane foam and other matrices. Nevertheless, increasing the graphene component to 2.5 wt.% and subsequently to 3 wt.% reduces the compressive strength of the hybrid composite compared to the pure RPUF material. This reduction might be attributed to the stiffness of the hybrid fillers and the increase in the brittleness of the final composites. The SEM images in Figures 1(c) and 1(d) show evident foam cell rupture at higher graphene loadings.

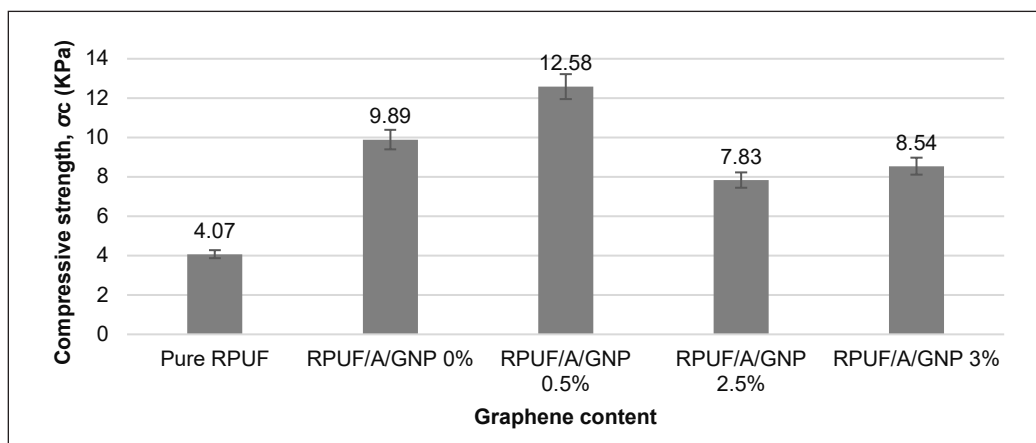


Figure 3. Compressive strength of pure RPUF and RPUF/ATH containing different graphene content

Fourier Transform Infrared (FTIR) Characterisation

FTIR spectroscopy is a versatile characterisation technique and a simple method for studying the formation of new bonds between polymers and nanoparticles or fillers in composites. This technique was employed to analyse virgin RPUF and RPUF/ATH-modified with and without graphene to observe any chemical reactions or the existence of new bonds in the materials. The FTIR spectra were acquired from 4000 to 500 cm^{-1} , as shown in Figure 4. The FTIR spectra revealed major IR vibration bands representing various oxygen-containing functional groups in the single and hybrid fillers. PU is a type of high polymer with a fundamental repeating unit of a urethane bond (-NHCOO-) manufactured by polymerising isocyanates and polyols (Mishra & Patel, 2020). Figure 4(a) shows the FTIR spectrum of the rigid PU foam in air at room temperature. The hydroxyl (OH) groups were observed at a wavenumber of 3,315 cm^{-1} , exhibiting wider peaks. The visible signals at 2,929 cm^{-1} and 2,358 cm^{-1} originate from symmetrical and asymmetrical stretch vibrations inside the CH_2 groups in the soft parts arising from polyols.

A prominent but relatively weak peak at 917 cm^{-1} , attributed to the symmetric stretching vibration of the N-CO-O bond and adsorption bands observed at approximately 765 cm^{-1} , indicates the presence of a C-H bond derived from an aromatic ring. The presence of carbonyl groups (C=O) at 1,709 cm^{-1} , N-H groups at 1,511 cm^{-1} (exhibiting a medium-strong peak), and hydrogen cyanide (C-N) at 1,221 cm^{-1} provided evidence for the establishment of urethane linkages (-RNHCOO-). Several researchers have reported these absorption bands (Alis et al., 2019; Wrzeźniewska-Tosik et al., 2020; Thiyagu et al., 2021). As shown in Figure 4(b), ATH was prepared using RPUF, and the composite was characterised by FTIR spectroscopy. The observed spectral bands of ATH were identified at 3,527 cm^{-1} , indicating the presence of hydroxyl (OH) group stretching. The hydroxyl groups on ATH react with the isocyanate group of the PU foam (Wang et al., 2017). In addition, the RPUF/

ATH peaks appear in the same position as the virgin RPUF. The Al-O and Al-O stretching and bending vibrations of ATH overlap those of RPUF with an increase in the strength of the peaks in the RPUF/ATH spectrum.

Hence, it can be asserted that the addition of ATH to RPUF did not produce significant changes in the strength of the bands observed in the foams. The pattern is similar to that in Figure 4(c), but the highest increase in the intensity of the C=O peaks ($3,734\text{ cm}^{-1}$) was recorded for the RPUF/0.5 wt.% graphene composite, matching the stretch vibrations of the amine (N-H) bond. Figure 4(c) also shows the slight effects of graphene on the spectra of the RPUF, demonstrating that it is difficult to detect the formation of urethane bonds between the RPUF and graphene because the PU backbones have the same chemical bonds. However, after the addition of graphene, there was a clear change in the intensity of the peaks of the composites. The strength of the peaks increases at $3,471\text{ cm}^{-1}$, $2,976\text{ cm}^{-1}$, $2,360\text{ cm}^{-1}$ (the second and third are ascribed to the alkene-CH stretch vibrations), $1,224\text{ cm}^{-1}$, and $1,067\text{ cm}^{-1}$ (attributed to C-O-C stretching vibrations). The increase in the intensity of the amide group (N-H) peak ($1,509\text{ cm}^{-1}$) indicates bending vibration (Hodlur & Rabinal,

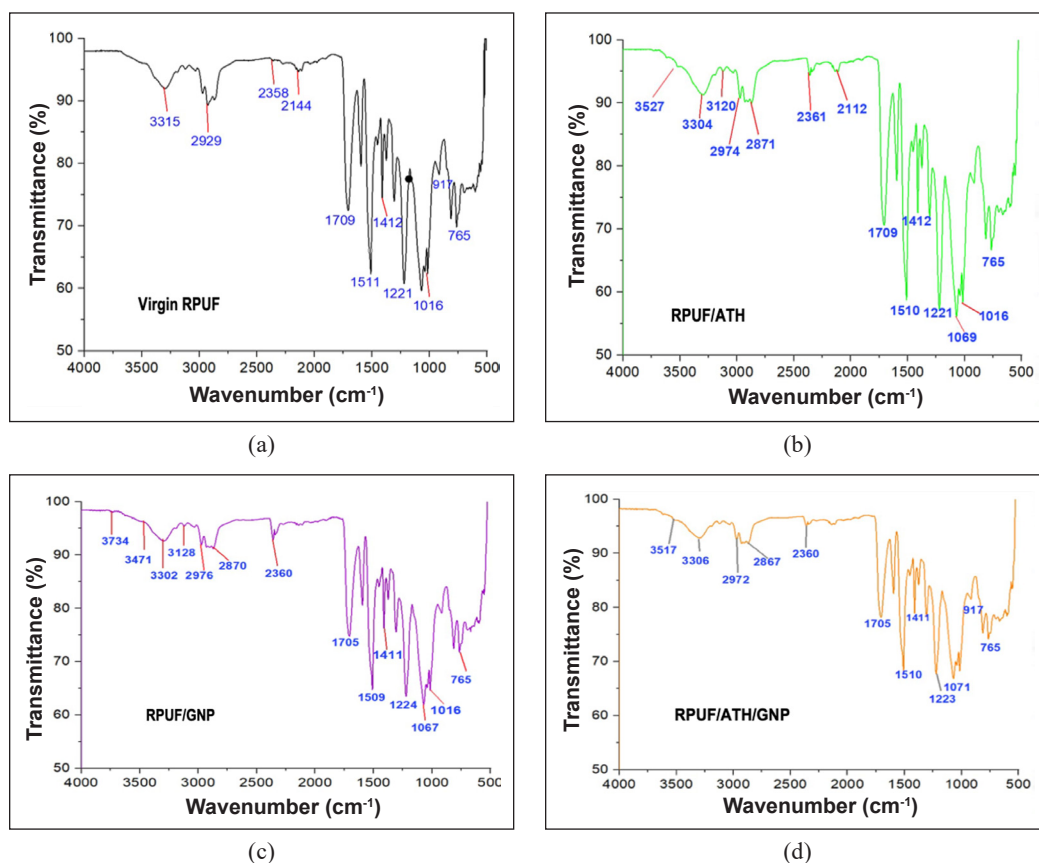


Figure 4. Infrared spectra: (a) Virgin RPUF; (b) RPUF/ATH; (c) RPUF/0.5 wt.% GNP; and (d) RPUF/ATH/0.5 wt.% GNP

2014). It suggests that the reaction between the -O-H and the NCO groups is catalysed by a combination of graphene and surfactant. The interface between the N and H bond of PU and the residual oxygenated groups of graphene was responsible for the disparity in the FT-IR spectra (Liu et al., 2017). Similar observations were reported in other studies on certain composites of RPUF and graphene (Gedam et al., 2019; Thiyagu et al., 2021). Figure 4(d) shows the FTIR spectra of the hybrid RPUF composites containing ATH and graphene fillers. Peaks related to virgin RPUF at $3,315\text{ cm}^{-1}$, $2,929\text{ cm}^{-1}$, $1,221\text{ cm}^{-1}$, and $1,016\text{ cm}^{-1}$ shifted to $3,517\text{ cm}^{-1}$, $2,972\text{ cm}^{-1}$, $1,223\text{ cm}^{-1}$, and $1,071\text{ cm}^{-1}$, respectively, owing to the interactions between ATH, graphene nanofiller, and polyurethane foam.

Many bands observed for virgin PU were also found in composites containing ATH, graphene, and surfactants. The band at $2,270\text{ cm}^{-1}$ was significant because it was missing in virgin PU and all its composites owing to the isocyanate (NCO) group. It proves that the entire supply of isocyanate was utilised to produce polyurethane (Pokharel et al., 2015). Due to the smaller quantity of graphene in the composite, obtaining solid evidence of physical or chemical interactions from the FTIR investigation was not easy. When the FTIR spectra of virgin RPUF were compared to those of its composites, no appreciable variation in the peak patterns was observed. Similar studies have reported comparable outcomes (Bera & Maji, 2017; Osman et al., 2021), demonstrating no filler matrix chemical interactions in the composites. All the chemical functional groups were unaltered because the filler was physically incorporated into the matrix.

Thermal Properties of RPUF and RPUF Hybrid Composites

Thorough comprehension of the flame retardancy mechanism requires analysis of the thermal characteristics during the combustion of RPUF-reinforced polyurethane foam (RPUF) and hybrid RPUF composites, which are commonly performed using thermogravimetric (TG) analysis. The thermal degradation of hybrid-reinforced polyurethane foam composites was examined using thermogravimetric analysis (TGA) and compared with the findings obtained for the virgin RPU foam. Table 3 lists the 5% mass loss temperature ($T_{5\%}$), the 50% mass loss temperature ($T_{50\%}$), the maximum degradation temperature (T_{max}), and the char residue at 800°C . The TGA and DTG thermograms of the virgin RPUF and hybrid RPUF foam composites are shown in Figures 5 and 6, respectively. The initial degradation temperature ($T_{5\%}$) of virgin RPUF was 23°C (Figure 5), and the release of volatile molecules, namely water molecules, was detected because of the high moisture uptake of the porous RPUF below 250°C .

In comparison, RPUF/ATH composites containing 0.5%, 2.5%, and 3.0 wt.% graphene, the $T_{5\%}$ values were 227°C , 253°C , and 256°C , respectively. It shows that increasing the amount of graphene in the RPUF improved the thermal firmness of the hybrid RPUF. It has been suggested that graphene slows the chain transfer reaction during the thermal

decomposition processes (Thiyagu et al., 2021). Generally, $T_{5\%}$, $T_{50\%}$, and T_{max} are higher for RPUF/graphene hybrid composites than for virgin RPUF, indicating the influence of graphene on enhancing the thermal stability of PU foam composites. For instance, while $T_{50\%}$ and T_{max} for RPUF/ATH were 334°C and 306°C, respectively, those of RPUF/ATH/graphene 0.5 wt.% were 539°C and 538°C, respectively. At the graphene loading of 3 wt.%, the hybrid composite reaches a maximum decomposition temperature of 592°C, representing a 50% and 48.3% increase in thermal stability compared to virgin RPUF (296°C) and RPUF/ATH (300°C). It is attributed to the high aspect ratio of graphene, which enables the formation of barricading layers and limits gaseous emissions during thermal degradation. The thermal stability of the RPUF hybrids was higher at a loading of 3.0 wt.% graphene, credited to the homogeneous and uniform dispersion of graphene.

Previous research has found that graphene sheets have a good barrier effect in preventing the transport of combustible decomposed products during the thermal degradation of composites and in slowing down the thermal decomposition process (Yuan et al., 2018). The initial breakdown of RPUF occurs within the temperature range of 231–424°C, attributed to the rupture of the urethane linkages. The second stage occurs at approximately 512–712°C and is ascribed to the cleavage of strong bonds such as aromatic groups, aliphatic carbon-carbon, and flame retardants (Kairytė et al., 2020). While the maximum degradation temperature (T_{max}) for virgin RPUF was observed to be 296°C, with a char residue of 15.18%, there was a significant increase in T_{max} for RPUF composites. For the case of RPUF/ATH composites, the T_{max} was 306°C, and the residual char reached 21.20%. The increases can be interpreted as an enhancement in thermal stability after the addition of ATH. These improvements can be attributed to the water molecules released from ATH. The presence of water molecules tends to cool the hot polymer, requiring a higher thermal energy to break down (Thirumal et al., 2010). In addition, water dilution reduces the concentration of combustible gases, and the development of a protective layer of aluminium oxide acts as a barrier, preventing the passage of oxygen and fuel into the polymers.

Figure 6 shows the DTG curves of the hybrid RPUF composites with different graphene concentrations. As observed, the RPUF/ATH/graphene hybrid composites displayed a shoulder peak, attributed to the removal of oxygen-containing complexes used in graphene

Table 3
Thermogravimetric data for pure RPUF and hybrid RPUF composites

Sample	T_5 (°C)	T_{50} (°C)	T_{max} (°C)	Char residue (%) at 800°C
Virgin RPUF	231	318	296	15.18
RPUF/A	278	334	306	21.20
RPUF/A/GNP 0.5%	227	539	538	15.50
RPUF/A/GNP 2.5%	253	579	547	16.66
RPUF/A/GNP 3.0%	256	591	592	17.46

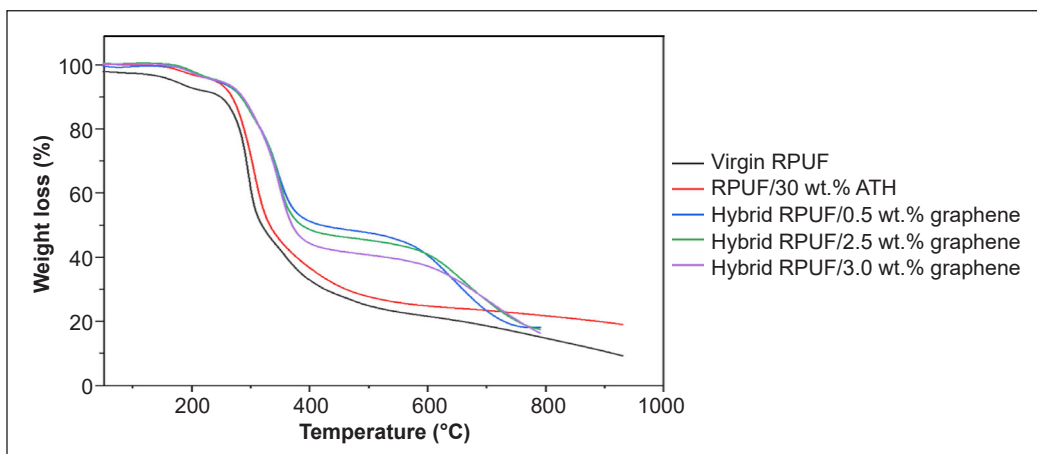


Figure 5. TGA curves of RPUF and hybrid RPUF with 0.5, 2.5, and 3.0 wt.% graphene

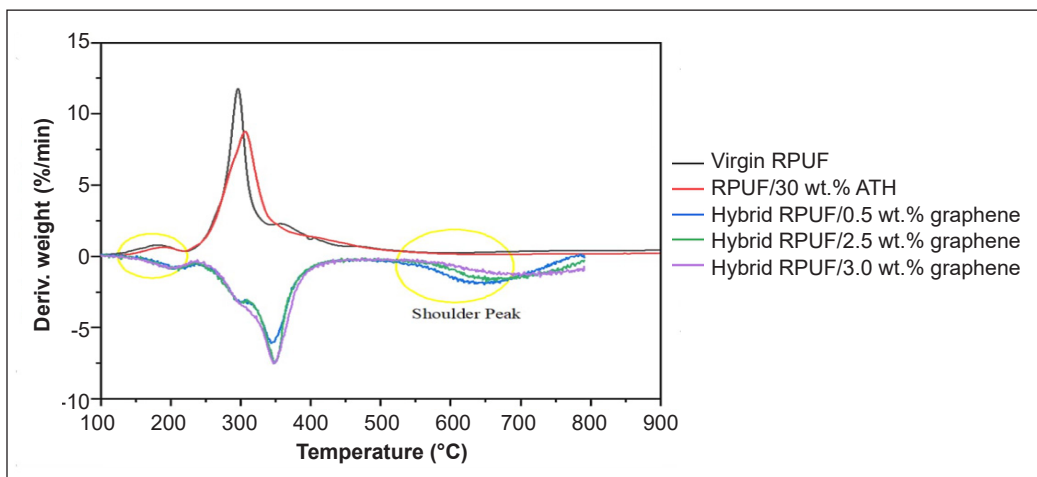


Figure 6. DTG curve for hybrid RPUF composites at different graphene concentrations

and ATH to enhance their dispersal in the polymer matrix. These changes were observed in the DTG thermograms, suggesting a notable reduction in the rate of mass loss during the second phase of thermal degradation in the system comprising all three graphene concentrations. At 2.5% and 3% graphene contents, the final stage of thermal degradation gradually diminished, indicating a significant quantity of solid residue ($> 20\%$). However, the decomposition temperatures for the last stage at 0.5%, 2.5%, and 3.0 wt.% graphene loading are 588°C , 613°C , and 672°C , respectively. The data in Table 3 reveal that the residual ash for the hybrid composites increases gradually with increasing graphene content. The emergence of chars impedes the transfer of heat, mass, and combustible gases at high temperatures, delaying the spontaneous scission of the polymer chain and increasing T_{max} (Huang et al., 2014).

The thermal stability of the RPUF/ATH composite increased to a higher decomposition temperature upon the addition of graphene, attributed to the better dispersion between graphene and ATH in the PU polymer system, as confirmed by the SEM results shown in Figure 1. During thermal degradation, adding graphene to the polymer system impedes the mass transfer of the generated volatile products (Zhu et al., 2021). This factor significantly improved the thermal stability of graphene-based materials. In other words, the thermal stability of the RPUF matrix increased after incorporating graphene loadings and ATH. This addition also improves the attraction and interface influence in the RPUF composites. These results align with previous studies that have shown the enhancement of thermal properties in polymer composites and their hybrids when graphene was used as a standalone filler or combined with other fillers (Sinh et al., 2019). Ultimately, these findings can be utilised to optimise the manufacturing process and produce high-quality hybrid rigid polyurethane composites with improved thermal stability. This cost-effective solution is promising for various industrial applications.

Fire Behaviour of ATH/Graphene Hybrid RPUF Composites

The LOI value was dependent on the surrounding temperature of the sample. The percentage of oxygen required for combustion decreased as the surrounding temperature increased. The LOI values of polymers and composites increase because of their ability to yield char in a fire, as char formation occurs at the expense of flammable volatiles (Chen et al., 2019). The fire-retardant behaviour of RPU foams was evaluated using the limiting oxygen index (LOI) and Underwriters Laboratories (UL-94) vertical burning test. The LOI assessment device was used to determine the percentage of oxygen volume required for polymer combustion, whereas the flammability of the specimens was assessed using a UL-94 vertical combustion analyser. The LOI value, burning time, ignition of the underlying cotton, and the UL-94 V classification during combustion are presented in Table 4. The Virgin RPUF exhibited an LOI value of 18% owing to its high flammability and low LOI value; the foam is highly flammable.

These substances readily evaporate at normal temperatures and release their components into the atmosphere. When heated, the chemicals ignite, causing the PU to burn. Virgin RPUF have poor fire response characteristics owing to their combustible hydrocarbon chains and high specific surface areas (Wang et al., 2019), which can be attributed to the significant amount of nitrogen in their structures. Typical PU foams emit highly poisonous smoke during combustion, particularly hydrogen cyanide (HCN) and carbon monoxide (CO) (Chattopadhyay & Webster, 2009). However, to impart non-flammable properties to virgin RPUF, the foam structure was modified by incorporating an organic flame retardant, such as aluminium hydroxide (ATH). As shown in Table 4, adding the 30 wt.% ATH to the virgin rigid PU foam increased the composite LOI value from 18% to 23% and achieved

a V-0 UL-94 test grade. This result indicates that the ATH-modified composite exhibits resistance to combustion with slow-burning characteristics. Composite materials with LOI values in the range of 21–27 tend to burn slowly, limiting their damage before the arrival of the fire rescue team (Fenimore, 1975)

The increase in the LOI value of RPUF/ATH can be attributed to ATH's fire-retardancy mechanism. ATH is an inorganic filler containing crystalline water in its chemical structure. During the endothermic reaction at (220–450°C), it releases approximately 34 wt.% steam. It reduces the composite temperature during combustion, and the released steam dilutes the combustible gases, resulting in an increased LOI. Additionally, ATH underwent a dehydration reaction, producing Al_2O_3 and carbonising the composites, as shown in Figure 7. It generates flammable volatiles and prevents the spread of flame (Wang et al., 2010; Zhu et al., 2014). As shown in Table 4, the incorporation of graphene into RPUF/ATH slightly decreased the LOI values for the hybrid RPUF composite compared with RPUF/ATH alone. The LOI values marginally decreased to 20% LOI for 0.5 wt.% graphene incorporation and 21% LOI for 2.5 wt.% graphene incorporation. Interestingly, at the graphene loading of 2.5 wt.%, the UL-94 test reveals a V-0 rating, and the burn time decreases to 10 s. It indicates a slight improvement in the flame resistance of the RPUF hybrid composite compared with that of the RPUF/ATH composite, which had a longer burn period of 16 s. However, for the 0.5% and 2.5 wt.% graphene-modified hybrid composites, the increase in their LOI values can be attributed to the dispersion state of the nanofiller, which has a noticeable effect on their reaction to small flames and fire behaviour under forced flaming conditions (Yuan et al., 2018). At a maximum graphene loading of 3.0 wt.%, the hybrid RPUF composite achieved an increased LOI value of 23%, indicating that a higher concentration of graphene, combined with other additives such as ATH, significantly enhances the fire resistance of the composites, confirming their synergistic flame-retardant effect.

Both graphene and ATH demonstrated better performance as hybrid flame retardants, as they can swell and block the spread of fire from the upper portion of the specimen to the bottom. All ATH and graphene-based flame-retardant blends exhibited higher LOI values than the virgin RPUF. This result demonstrates that the combination of ATH and graphene has a favourable impact, enhancing the fire characteristics of pristine RPUF. It was attributed to the synergistic effect of ATH/graphene at high filler contents. Graphene disperses heat within the samples (Dittrich et al., 2013), while ATH reduces the release of combustible gases by releasing water (Hull et al., 2011) and, in significant amounts, delays the combustion of the materials by reducing the availability of combustible fuel from the virgin RPUF. This finding is consistent with previous studies indicating that graphene, with its two-dimensional layered structure, can enhance polymer char formation during combustion by accumulating and re-irradiating heat (Han et al., 2013; Han et al., 2014). The combination of ATH with graphene and another flame retardant as a hybrid filler has

improved the fire behaviour of various hybrid polymer composites, making them suitable for use in high-performance engineering applications (Battig et al., 2021; Wang et al., 2017; Zielonka et al., 2022).

Table 4
Results of UL-94 and LOI test of hybrid RPUF composites incorporated with ATH and various quantities of graphene

Samples	Graphene Loading (wt.%)	Burn time (s)	Ignition of cotton	UL-94 Classification	LOI (%)
Virgin RPUF	0	25	YES	Failed	18
RPUF/A	0	16	NO	V-1	19
RPUF/A/GNP	0.5	16	NO	V-1	20
RPUF/A/GNP	2.5	10	NO	V-0	21
RPUF/A/GNP	3.0	8	NO	V-0	23

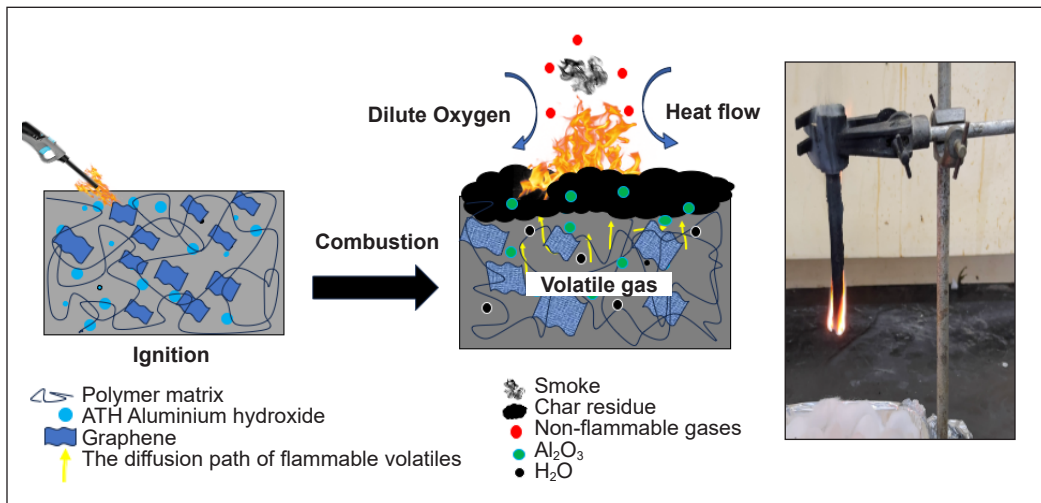


Figure 7. Schematic illustration of the flame retardant mechanism of ATH/graphene system in RPUF

CONCLUSION

This study successfully modified rigid polyurethane foams (RPUF) with aluminium hydroxide (ATH) and graphene to enhance their compressive strength, flame retardancy, and thermal properties. The addition of ATH and graphene to RPUF resulted in the development of synergistic effects, leading to improved performance of the hybrid composites. The results indicate that the incorporation of 0.5 wt.% graphene loading in the hybrid composite exhibited the best compression performance, with a compressive strength value of 12.58 KPa, surpassing both virgin RPUF (4.07 KPa) and RPUF/ATH (9.89 KPa). This enhancement in compressive strength can be attributed to the reinforcing

effects of ATH and graphene, which effectively distribute stress and improve the overall structural integrity of the hybrid composite. The characterisation of the hybrid composites using SEM micrographs revealed a more stable and uniform structure with the addition of 0.5 wt.% graphene. Infrared spectral analysis confirmed the presence of functional groups in the virgin RPUF and some modified composites, indicating the successful incorporation of ATH and graphene into the RPUF matrix. Thermal analysis demonstrated that the hybrid composites exhibited improved thermal stability compared to the virgin RPUF. The addition of 3.0 wt.% graphene resulted in a significant increase in the maximum decomposition temperature (539°C) and char residue (17.46%). These findings suggest that graphene is crucial in enhancing the hybrid composites' thermal stability and flame retardancy. Furthermore, LOI and UL-94 analyses revealed that the hybrid composites incorporated with 3.0 wt.% graphene exhibited increased LOI value and achieved V-0 classification, indicating enhanced fire resistance compared to the virgin samples. The hybrid composite is a promising material for high-performance applications, particularly building insulation. In summary, incorporating aluminium hydroxide and graphene into RPUF led to developing hybrid composites with improved compressive strength, thermal stability, and flame retardancy. The synergistic effects of ATH and graphene contributed to the enhanced properties of the hybrid composites. These findings contribute to the advancement of materials science and provide insight into developing novel flame-retardant RPUF composites for various industrial applications.

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REFERENCES

- Alis, A., Majid, R. A., & Mohamad, Z. (2019). Morphologies and thermal properties of palm-oil based rigid polyurethane/halloysite nanocomposite foams. *Journal-Chemical Engineering Transactions*, 72, 415–420. <http://doi.org/10.3303/CET1972070>
- American Society for Testing and Materials. (2001). *Standard test method for compressive properties of rigid cellular plastics* (ASTM D1621-1). ASTM International.
- American Society for Testing and Materials. (1997). *Standard test Method for measuring the minimum oxygen concentration to support candle-like combustion of plastics (oxygen index)* (ASTM D2863-97). ASTM International.
- American Society for Testing and Materials. (2010). *Standard test method for measuring the comparative burning characteristics of solid plastics in a vertical position* (ASTM D3801-10). ASTM International.

- Baferani, A. H., Keshavarz, R., Asadi, M., & Ohadi, A. R. (2018). Effects of silicone surfactant on the properties of open-cell flexible polyurethane foams. *Advances in Polymer Technology*, 37(1), 71–83. <https://doi.org/10.1002/adv.21643>
- Baguian, A. F., Ouiminga, S. K., Longuet, C., Caro-Bretelle, A. S., Corn, S., Bere, A., & Sonnier, R. (2021). Influence of density on foam collapse under burning. *Polymers*, 23(1), Article 13. <https://dx.doi.org/10.3390/polym13010013>
- Battig, A., Fadul, N. A. R., Frasca, D., Schulze, D., & Schartel, B. (2021). Multifunctional graphene nanofiller in flame retarded polybutadiene/chloroprene/carbon black composites. *e-Polymers*, 21(1), 244–262. <https://doi.org/10.1515/epoly-2021-0026>
- Bera, M., & Maji, P. K. (2017). Effect of structural disparity of graphene-based materials on thermo-mechanical and surface properties of thermoplastic polyurethane nanocomposites. *Polymer*, 119, 118–133. <https://doi.org/10.1016/j.polymer.2017.05.019>
- Chattopadhyay, D. K., & Webster, D. C. (2009). Thermal stability and flame retardancy of polyurethanes. *Progress in Polymer Science*, 34(10), 1068–1133. <https://doi.org/10.1016/j.progpolymsci.2009.06.002>
- Chen, M. J., Xu, Y. J., Rao, W. H., Huang, J. Q., Wang, X. L., Chen, L., & Wang, Y. Z. (2014). Influence of valence and structure of phosphorus-containing melamine salts on the decomposition and fire behaviours of flexible polyurethane foams. *Industrial and Engineering Chemistry Research*, 53(21), 8773–8783. <https://doi.org/10.1021/ie500691p>
- Chen, X. Y., Huang, Z. H., Xi, X. Q., Li, J., Fan, X. Y. & Wang, Z. (2018). Synergistic effect of carbon and phosphorus flame retardants in rigid polyurethane foams. *Fire and Materials*, 42(4), 447–453. <https://doi.org/10.1002/fam.2511>
- Chen, X. Y., Romero, A., Paton-Carrero, A., Lavin-Lopez, M. P., Sanchez-Silva, L., Valverde, J. L., Kaliaguine, S., & Rodrigue, D. (2019). Functionalized graphene–reinforced foams based on polymer matrices. In M. Jawaid, R. Bouhfid & A. K. Quaiss (Eds.), *Functionalized Graphene Nanocomposites and their Derivatives* (pp. 121-155). Elsevier. <https://doi.org/10.1016/B978-0-12-814548-7.00007-6>
- Chen, X., Li, J., & Gao, M. (2019). Thermal degradation and flame retardant mechanism of the rigid polyurethane foam including functionalized graphene oxide. *Polymers*, 11(1), Article 78. <https://www.mdpi.com/2073-4360/11/1/78>
- Cheng, J. J., Shi, B. B., Zhou, F. B., & Chen, X. Y. (2014). Effects of inorganic fillers on the flame-retardant and mechanical properties of rigid polyurethane foams. *Journal of Applied Polymer Science*, 131(10), Article 40253. <https://doi.org/10.1002/app.40253>
- Członka, S., Kairyte, A., Miedzińska, K., Strakowska, A., & Adamus-Włodarczyk, A. (2021). Mechanically strong polyurethane composites reinforced with montmorillonite-modified sage filler (*Salvia officinalis* L.). *International Journal of Molecular Sciences*, 22(7), Article 3744. <https://doi.org/10.3390/ijms22073744>
- Dhaliwal, G. S., Anandan, S., Bose, M., Chandrashekhara, K., & Nam, P. (2020). Effects of surfactants on mechanical and thermal properties of soy-based polyurethane foams. *Journal of Cellular Plastics*. 56(6), 611–629. <https://doi.org/10.1177/0021955X20912200>
- Dittrich, B., Wartig, K. A., Hofmann, D., Mülhaupt, R., & Schartel, B. (2013). Flame retardancy through carbon nanomaterials: Carbon black, multiwall nanotubes, expanded graphite, multi-layer graphene

- and graphene in polypropylene. *Polymer Degradation and Stability*, 98(8), 1495–1505. <https://doi.org/10.1016/j.polyimdegradstab.2013.04.009>
- Eaves, D. (2004). *Handbook of polymer foams*. Rapra Technology Ltd.
- Eling, B., Tomović, Ž., & Schädler, V. (2020). Current and future trends in polyurethanes: An industrial perspective. *Macromolecular Chemistry and Physics*, 221(14), Article 2000114. <https://doi.org/10.1002/macp.202000114>
- Feng, C., Liang, M., Zhang, Y., Jiang, J., Huang, J., & Liu, H. (2016). Journal of analytical and applied pyrolysis synergistic effect of lanthanum oxide on the flame retardant properties and mechanism of an intumescent flame retardant PLA composites. *Journal of Analytical and Applied Pyrolysis*, 122, 241–248. <https://doi.org/10.1016/j.jaap.2016.09.018>
- Fenimore, C. P. (1975). Candle-type test for flammability of polymers. In M. Lewin, S. M. Atlas & E. M. Pearce (Eds.), *Flame-Retardant Polymeric Materials* (pp. 259-267). Springer. https://doi.org/10.1007/978-1-4684-2148-4_9
- Gedam, S. S., Chaudhary, A. K., Vijayakumar, R. P., Goswami, A. K., Bajad, G. S., & Pal, D. (2019). Thermal, mechanical and morphological study of carbon nanotubes-graphene oxide and silver nanoparticles based polyurethane composites. *Materials Research Express*, 6(8), Article 085308. <https://doi.org/10.1088/2053-1591/ab1db4>
- Han, Y., Wu, Y., Shen, M., Huang, X., Zhu, J., & Zhang, X. (2013). Preparation and properties of polystyrene nanocomposites with graphite oxide and graphene as flame retardants. *Journal of Materials Science*, 48(12), 4214–4222. <https://doi.org/10.1007/s10853-013-7234-8>
- Han, Z., Wang, Y., Dong, W., & Wang, P. (2014). Enhanced fire retardancy of polyethylene/alumina trihydrate composites by graphene nanoplatelets. *Materials Letters*, 128, 275–278. <https://doi.org/10.1016/j.matlet.2014.04.148>
- Hodlur, R. M., & Rabinal, M. K. (2014). Self assembled graphene layers on polyurethane foam as a highly pressure sensitive conducting composite. *Composites Science and Technology*, 90, 160–165. <https://doi.org/10.1016/j.compscitech.2013.11.005>
- Huang, G., Chen, S., Song, P., Lu, P., Wu, C., & Liang, H. (2014). Combination effects of graphene and layered double hydroxides on intumescent flame-retardant poly (methyl methacrylate) nanocomposites. *Applied Clay Science*, 88–89, 78–85. <https://doi.org/10.1016/j.clay.2013.11.002>
- Huang, S., Deng, C., Zhao, Z., Chen, H., Gao, Y., & Wang, Y. (2020). Phosphorus-containing organic-inorganic hybrid nanoparticles for the smoke suppression and flame retardancy of thermoplastic polyurethane. *Polymer Degradation and Stability*, 178, Article 109179. <https://doi.org/10.1016/j.polyimdegradstab.2020.109179>
- Hull, T. R., Witkowski, A., & Hollingbery, L. (2011). Fire retardant action of mineral fillers. *Polymer Degradation and Stability*, 96(8), 1462–1469. <https://doi.org/10.1016/j.polyimdegradstab.2011.05.006>
- Jeśiak, T., Hasiak, M., Łaszcz, A., Chęćmanowski, J., Gerasymchuk, Y., Stachowiak, P., Strek, W., & Hreniak, D. (2023). Thermo-smart composite materials: Exploring the potential of graphene-doped porous silica foams. *Construction and Building Materials*, 394, Article 132249. <https://doi.org/10.1016/j.conbuildmat.2023.132249>

- Jonjaroen, V., Ummartyotin, S., & Chittapun, S. (2020). Algal cellulose as a reinforcement in rigid polyurethane foam. *Algal Research*, 51, Article 102057. <https://doi.org/10.1016/j.algal.2020.102057>
- Ju, Z., He, Q., Zhang, H., Zhan, T., Chen, L., Li, S., Hong, L., & Lu, X. (2020). Steam explosion of windmill palm fibre as the filler to improve the acoustic property of rigid polyurethane foams. *Polymer Composites*, 41(7), 2893–2906. <https://doi.org/10.1002/pc.25585>
- Kairytė, A., Kremensas, A., Balčiūnas, G., Członka, S., & Strażowska, A. (2020). Closed cell rigid polyurethane foams based on low functionality polyols: Research of dimensional stability and standardised performance properties. *Materials*, 13(6), Article 1438. <https://doi.org/10.3390/ma13061438>
- Kavšek, M., Figar, N., Mihelič, I., & Krajnc, M. (2022). Melamine-formaldehyde rigid foams – Manufacturing and their thermal insulation properties. *Journal of Cellular Plastics*, 58(1), 175–193. <https://doi.org/10.1177/0021955X21997348>
- Kerche, E. F., Delucis, R. D. A., Petzhold, C. L., & Amico, S. C. (2020). Rigid bio-based wood/polyurethane foam composites expanded under confinement. *Journal of Cellular Plastics*, 57(5), 757–768. <https://doi.org/10.1177/0021955X20964018>
- Kim, J. M., Kim, D. H., Kim, J., Lee, J. W., & Kim, W. N. (2017). Effect of graphene on the sound damping properties of flexible polyurethane foams. *Macromolecular Research*, 25(2), 190–196. <https://doi.org/10.1007/s13233-017-5017-9>
- Kumar, M., & Kaur, R. (2017). Glass fibre reinforced rigid polyurethane foam: Synthesis and characterisation. *E-Polymers*, 17(6), 517–521. <https://doi.org/10.1515/epoly-2017-0072>
- Lee, C., Wei, X., Kysar, J. W., & Hone, J. (2008). Measurement of the elastic properties and intrinsic strength of monolayer graphene. *Science*, 321(5887), 385–388. <https://doi.org/10.1126/science.1157996>
- Lee, S. H., Lee, S. G., Lee, J. S., & Ma, B. C. (2022). Understanding the flame retardant mechanism of intumescent flame retardant on improving the fire safety of rigid polyurethane foam. *Polymers*, 14(22), Article 4904. <https://doi.org/10.3390/polym14224904>
- Liu, D., & Hu, A. (2020). The influence of environmentally friendly flame retardants on the thermal stability of phase change polyurethane foams. *Materials*, 13(3), Article 520. <https://doi.org/10.3390/ma13030520>
- Liu, D., Zou, L., Chang, Q., & Xiao, T. (2021). Preparation and properties of rigid polyurethane foams added with graphene oxide-hollow glass microspheres hybrid. *Designed Monomers and Polymers*, 24(1), 210–217. <https://doi.org/10.1080/15685551.2021.1954340>
- Liu, H., Dong, M., Huang, W., Gao, J., Dai, K., Guo, J., Zheng, G., Liu, C., Shen, C., & Guo, Z. (2017). Lightweight conductive graphene/thermoplastic polyurethane foams with ultrahigh compressibility for piezoresistive sensing. *Journal of Materials Chemistry C*, 5(1), 73–83. <https://doi.org/10.1039/C6TC03713E>
- Liu, X., Hao, J., & Gaan, S. (2016). Recent studies on the decomposition and strategies of smoke and toxicity suppression for polyurethane-based materials. *RSC Advances*, 6(78), 74742–74756. [10.1039/C6RA14345H](https://doi.org/10.1039/C6RA14345H)
- Lorusso, C., Vergaro, V., Conciauro, F., Ciccarella, G., & Congedo, P. M. (2017). Thermal and mechanical performance of rigid polyurethane foam added with commercial nanoparticles. *Nanomaterials and Nanotechnology*, 7(1–19), Article 184798041668411. <https://doi.org/10.1177/1847980416684117>

- Mishra, V. K., & Patel, R. H. (2020). Synthesis and characterization of flame retardant polyurethane: Effect of castor oil polyurethane on its properties. *Polymer Degradation and Stability*, 175, Article 109132. <https://doi.org/10.1016/j.polymdegradstab.2020.109132>
- Modesti, M., Lorenzetti, A., Simioni, F., & Camino, G. (2002). Expandable graphite as an intumescent flame retardant in polyisocyanurate-polyurethane foams. *Polymer Degradation and Stability*, 77(2), 195–202. [https://doi.org/10.1016/S0141-3910\(02\)00034-4](https://doi.org/10.1016/S0141-3910(02)00034-4)
- Mohamad, Z., Raji, A. M., Hassan, A., & Khan, Z. I. (2021). Novel intumescent flame retardant of ammonium polyphosphate/sepiolite/melamine on rigid polyurethane foam: Morphologies, and flammability properties. *Chemical Engineering Transactions*, 89, 619–624. <https://doi.org/10.3303/CET2189104>
- Osman, A., Elhakeem, A., Kaytbay, S., & Ahmed, A. (2021). Thermal , electrical and mechanical properties of graphene / nano-alumina / epoxy composites. *Materials Chemistry and Physics*, 257, Article 123809. <https://doi.org/10.1016/j.matchemphys.2020.123809>
- Pang, H., Wu, Y., Wang, X., Hu, B., & Wang, X. (2019). Recent advances in composites of graphene and layered double hydroxides for water remediation: A review. *Chemistry – An Asian Journal*, 14(15), 2542–2552. <https://doi.org/10.1002/asia.201900493>
- Peng, H., Wang, X., Li, T., Lou, C., Wang, Y., & Lin, J. (2019). Mechanical properties, thermal stability, sound absorption, and flame retardancy of rigid PU foam composites containing a fire-retarding agent: Effect of magnesium hydroxide and aluminium hydroxide. *Polymers for Advanced Technologies*, 30(8), 2045–2055. <https://doi.org/10.1002/pat.4637>
- Pinto, S. C., Marques, P. A. A. P., Vicente, R., Godinho, L., & Duarte, I. (2020). Hybrid structures made of polyurethane/graphene nanocomposite foams embedded within aluminum open-cell foam. *Metals*, 10(6), Article 768. <https://doi.org/10.3390/met10060768>
- Pokharel, P., Choi, S., & Lee, D. S. (2015). The effect of hard segment length on the thermal and mechanical properties of polyurethane/graphene oxide nanocomposites. *Composites Part A*, 69, 168–177. <https://doi.org/10.1016/j.compositesa.2014.11.010>
- Rocha, J. D. S., Escócio, V. A., Visconte, L. L. Y., & Pacheco, É. B. A. V. (2021). Thermal and flammability properties of polyethylene composites with fibers to replace natural wood. *Journal of Reinforced Plastics and Composites*, 40(19–20), 726–740. <https://doi.org/10.1177/07316844211002895>
- Salasińska, K., Leszczyńska, M., Celiński, M., Kozikowski, P., Kowiorski, K., & Lipińska, L. (2021). Burning behaviour of rigid polyurethane foams with histidine and modified graphene oxide. *Materials*, 14(5), Article 1184. <https://doi.org/10.3390/ma14051184>
- Shivakumar, H., Renukappa, N. M., Shivakumar, K. N., & Suresha, B. (2020). The reinforcing effect of graphene on the mechanical properties of carbon-epoxy composites. *Open Journal of Composite Materials*, 10(02), 27–44. <https://doi.org/10.4236/ojcm.2020.102003>
- Shoaib, S., Shahzad Maqsood, K., Nafisa, G., Waqas, A., Muhammad, S., & Tahir, J. (2014). A comprehensive short review on polyurethane foam. *International Journal of Innovation and Applied Studies*, 12(1), 165–169.
- Silva, E. H. P., Aguiar, J. C. F., Waldow, G., Costa, R. R. C., Tita, V., & Ribeiro, M. L. (2022). Compression and morphological properties of a bio-based polyurethane foam with aluminum hydroxide. *Proceedings of*

the Institution of Mechanical Engineers, Part L: Journal of Materials: Design and Applications, 236(7), 1408-1418. <https://doi.org/10.1177/14644207211059077>

- Sinh, L. H., Luong, N. D., & Seppälä, J. (2019). Enhanced mechanical and thermal properties of polyurethane/functionalised graphene oxide composites by in situ polymerisation. *Plastics, Rubber and Composites*, 48(10), 466–476. <https://doi.org/10.1080/14658011.2019.1664820>.
- Srihanum, A., Noor, M. T. T., Devi, K. P. P., Hoong, S. S., Ain, N. H., Mohd, N. S., Din, N. S. M. N. M., & Kian, Y. S. (2022). Low-density rigid polyurethane foam incorporated with renewable polyol as sustainable thermal insulation material. *Journal of Cellular Plastics*, 58(3), 485-503. <https://doi.org/10.1177/0021955X211062630>
- Stoller, M. D., Park, S., Yanwu, Z., An, J., & Ruoff, R. S. (2008). Graphene-based ultracapacitors. *Nano Letters*, 8(10), 3498–3502. <https://doi.org/10.1021/nl802558y>
- Thirumal, M., Singha, N. K., Khastgir, D., Manjunath, B. S., & Naik, Y. P. (2010). Halogen-free flame-retardant rigid polyurethane foams: Effect of alumina trihydrate and triphenylphosphate on the properties of polyurethane foams. *Journal of Applied Polymer Science*, 116(4), 2260–2268. <https://doi.org/10.1002/app.31626>
- Thiyagu, C., Manjubala, I., & Narendrakumar, U. (2021). Thermal and morphological study of graphene-based polyurethane composites. *Materials Today: Proceedings*, 45, 3982–3985. <https://doi.org/10.1016/j.matpr.2020.08.641>
- Titow, W. V. (2001). *PVC Technology*, 146. Rapra Technology Ltd.
- Tiuc, A. E., Borlea, S. I., Nemeş, O., Vermeşan, H., Vasile, O., Popa, F., & Pinţoi, R. (2022). New composite materials made from rigid/flexible polyurethane foams with fir sawdust: Acoustic and thermal behavior. *Polymers*, 14(17), Article 3643. <https://doi.org/10.3390/polym14173643>
- Wang, S., Du, X., Jiang, Y., Xu, J., Zhou, M., Wang, H., Cheng, X., & Du, Z. (2019). Synergetic enhancement of mechanical and fire-resistance performance of waterborne polyurethane by introducing two kinds of phosphorus–nitrogen flame retardant. *Journal of colloid and interface science*, 537, 197-205. <https://doi.org/10.1016/j.jcis.2018.11.003>
- Wang, Y., Wang, F., Dong, Q., Xie, M., Liu, P., Ding, Y., Zhang, S., Yang, M., & Zheng, G. (2017). Core-shell expandable graphite @ aluminum hydroxide as a flame-retardant for rigid polyurethane foams. *Polymer Degradation and Stability*, 146, 267–276. <https://doi.org/10.1016/j.polyimdegradstab.2017.10.017>
- Wang, Y., Wang, F., Dong, Q., Yuan, W., Liu, P., Ding, Y., Zhang, S., Yang, M., & Zheng, G. (2018). Expandable graphite encapsulated by magnesium hydroxide nanosheets as an intumescent flame retardant for rigid polyurethane foams. *Journal of Applied Polymer Science*, 135(39), Article 46749. <https://doi.org/10.1002/app.46749>
- Wang, Z. Y., Liu, Y., & Wang, Q. (2010). Flame retardant polyoxymethylene with aluminium hydroxide/melamine/novolac resin synergistic system. *Polymer Degradation and Stability*, 95(6), 945–954. <https://doi.org/10.1016/j.polyimdegradstab.2010.03.028>
- Wrześniewska-Tosik, K., Ryszkowska, J., Mik, T., Wesołowska, E., Kowalewski, T., Pałczyńska, M., Sałasińska, K., Walisiak, D., & Czajka, A. (2020). Composites of semi-rigid polyurethane foams with keratin fibers

- derived from poultry feathers and flame retardant additives. *Polymers*, 12(12), Article 2943. <https://doi.org/10.3390/polym12122943>
- Yao, Y., Jin, S., Ma, X., Yu, R., Zou, H., Wang, H., Lv, X., & Shu, Q. (2020). Graphene-containing flexible polyurethane porous composites with improved electromagnetic shielding and flame retardancy. *Composites Science and Technology*, 200, Article 108457. <https://doi.org/10.1016/j.compscitech.2020.108457>
- Yuan, B., Sun, Y., Chen, X., Shi, Y., Dai, H., & He, S. (2018). Poorly-/well-dispersed graphene: Abnormal influence on flammability and fire behaviour of intumescent flame retardant. *Composites Part A: Applied Science and Manufacturing*, 109, 345–354. <https://doi.org/10.1016/j.compositesa.2018.03.022>
- Zhang, W., Zhao, Z., & Lei, Y. (2021). Flame retardant and smoke-suppressant rigid polyurethane foam based on sodium alginate and aluminium diethyl phosphite. *Designed Monomers and Polymers*, 24(1), 46–52. <https://doi.org/10.1080/15685551.2021.1879451>
- Zhang, X., Sun, S., Yuan, D., Wang, Z., Xie, H., & Liu, Y. (2023). Fabrication of hydrolyzed keratin-modified rigid polyurethane foams and their thermal stability and combustion performance. *International Journal of Polymer Analysis and Characterization*, 28(7), 662-683. <https://doi.org/10.1002/pi.6616>
- Zhou, X., Jiang, F., Hu, Z., Wu, F., Gao, M., Chai, Z., Wang, Y., Gu, X., & Wang, Y. (2023). Study on the flame retardancy of rigid polyurethane foam with phytic acid-functionalized graphene oxide. *Molecules*, 28(17), Article 6267. <https://doi.org/10.3390/molecules28176267>
- Zhu, H., Peng, Z., Chen, Y., Li, G., Wang, L., Tang, Y., Pang, R., Khan, Z. U. H., & Wan, P. (2014). Preparation and characterization of flame retardant polyurethane foams containing phosphorus-nitrogen-functionalized lignin. *RSC Advances*, 4(98), 55271–55279. <https://doi.org/10.1039/C4RA08429B>
- Zhu, Q., Wang, Z., Zeng, H., Yang, T., & Wang, X. (2021). Effects of graphene on various properties and applications of silicone rubber and silicone resin. *Composites Part A: Applied Science and Manufacturing*, 142, Article 106240. <https://doi.org/10.1016/j.compositesa.2020.106240>
- Zielonka, P., Duda, S., Lesiuk, G., Błażejowski, W., Wiśniewska, M., Warycha, J., Stabla, P., Smolnicki, M., & Babiarczuk, B. (2022). The effect of flame retardant—Aluminum trihydroxide on mixed mode I/II fracture toughness of epoxy resin. *Polymers*, 14(20), Article 4386. <https://doi.org/10.3390/polym14204386>

