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Novel Intumescent Flame Retardant of Ammonium Polyphosphate/Sepiolite/Melamine on Rigid Polyurethane Foam: Morphologies, and Flammability Properties

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Rigid polyurethane (RPU) foams have been effectively modified with various intumescent flame retardants (IFR) of ammonium polyphosphate/sepiolite/melamine. This study aims to examine the morphologies and fire behaviour of RPU foams by exploring the potential of sepiolite as a novel carbonizing agent in an IFRs system. The effect of various amounts of IFR constituents on RPU foams was investigated. SEM images showed a more stable structure and lesser cell size in the RPUF composite with the incorporation of IFRs compared to that of pure RPUF. The results of the limiting oxygen index (LOI) test showed that 16 phr IFR in a mass ratio of 1:2:1 enhanced the LOI value of the composite by 23.20 % compared to pure RPUF. From the UL-94 analysis, the grade V-0 was obtained for RPUF/IFR 16 phr (1:2:1) and the lowest after-flame time after ignition of 21.4 s was recorded at this formulation compared to other IFR ratio and content used. All IFR components were observed to have contributed to the boosted flame retardancy of the RPUF. The findings of this study confirm that IFRs of ammonium polyphosphate/sepiolite/melamine enhance the interaction between the IFR and the foam matrix and have boosted the flame retardancy of RPU foam composites. There is a strong potential that the RPUF composite developed can be used as insulation material.

1. Introduction

Polyurethane (PU) is highly flammable as it releases toxic gases such as carbon monoxide (CO) during burning linked to polyol, one of its main components and this limit its use in structural applications, electronics (Gavgani et al., 2014) and transportation (Zieleniewska et al., 2015). In these sectors, flame retardants (FR) features are imperative and mandatory. In particular, PU primary market is PU foam, and PU foam synthesis has different foaming systems. The two main types of PU foam are flexible foam and rigid foam (Shoaib et al., 2014). Rigid polyurethane foam (RPUF) has the largest market share of 50 % of all PU foam as at the year 2020 (Zhou et al., 2020) and it is a kind of polymer-based foam containing carbamate groups in its main chain (Akindoyo et al., 2016). RPUF is extremely combustible with a below standard limiting oxygen index (LOI) value near 18 % (Li et al., 2018). Thus, a fire outbreak burns quickly with a rapid flame spread due to porous structure, low thermal inertia, large surface area, etc. Due to this, poisonous gases such as hydrogen cyanide (HCN) and carbon monoxide (CO) are released (Baguian et al., 2021). When inhaled, the released gas is a threat to human health during combustion (Zhou et al., 2020). Hence, it is mandatory to strengthen RPUF with FR to boost their fire retardancy and smoke suppressing property (Cao et al., 2017). Popular FR's such as halogen-containing compounds provides excellent flame retardation to RPUF; but they are not environmentally sustainable owing to issue of toxic gases in combustion (Bhoyate et al., 2018). Hence, the continuous demand for FR additives with high flame retardance efficiency that rarely pollutes the environment (Chen et al., 2012) for RPUF. The demand for halogen-free FRs has increased rapidly (Covaci et al., 2020), prompting the design of new FRs such as intumescent flame retardants (IFR) (Bhoyate et al., 2018). The IFR polymer system generally encompasses three constituents: an acid source, a carbon source, as well as a blowing/swelling agent. The carbon source is vital for charring and material surface isolation from heat and flames. The acid is employed to enhance compatibility between polymer components and contribute to char formation. The blowing agent breaks down

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in the presence of heat to allow the charred layer to swell (Alongi et al., 2015). Ammonium polyphosphate (APP), melamine (MEL), and pentaerythritol (PER), are the most popular commercial IFR system. There are deficiencies in this IFR system primarily in enhancing selected properties of RPUF (Baguian et al., 2021), for example, low (flame retardance efficacy, water-resistance and thermal stability) and their low compatibility with RPUF. So, from past studies, organic carbonizing agents (such as PER, melamine polyphosphate, and sorbitol) in the IFR system are popular; but they are expensive, not eco-friendly, and water-soluble nature lowered the flame retardancy of RPU foam (Wu et al., 2014). Ciecierska et al. (2016) described that IFRs could exhibit low compatibility with RPUF, especially at high loading (>25 phr), leading to reduced mechanical and other properties. Hence, there is a need to design a low content IFR formulations with good compatibility for RPUF. Sepiolite (SEP), a layered silicate and nanoclay, is proposed as a novel inorganic carbonizing agent in the IFR system. SEP clays are found naturally and cost-effective, among other unique attributes, making them attractive to use (Sabzi et al., 2020). Few researchers have synthesized or examined flame-FR and IFR rigid polyurethane foams (IFR-RPUF). Some of the most recent are RPUF/SEP (Wang et al., 2012), IFR PU/reduced graphene oxide (rGO) Composites (Gavgani,2014), RPUF/IFR (APP/MEL) composites (Yurtseven,2019), FR RPUF containing graphene oxide/EG/dimethyl methyl phosphate (DMMP) (Chen et al., 2019), FR RPUF by combining the influence of APP/DMMP (Zhu and Xu, 2020), and green FR of MEL/silica/ionic liquid for RPUF (Członka et al., 2020). No work is reported on the synthesis of an IFR formulation based on APP (acid source), SEP nanoclay (carbon source), MEL (swelling agent) and their impact on the morphology, and flammability properties of RPUF or any other polymer network. Therefore, this study aims to formulate a novel IFR system of APP/SEP/MEL at IFR loadings of 20 parts per hundred (phr) and 16 parts per hundred (phr) and incorporate it into RPUF. The IFR content employed in this study is below the average 25-30 phr IFR content used in previous studies.

2. Experimental

2.1 Materials

This study aims to develop eco-friendly IFR with APP, SEP, and MEL. Rigid polyurethane foams (RPUFs) were formed through the two-component system (Part A and Part B). The IFR mass ratios used was 1:2:1 and 1:1:1. Polyol 4500 series, Part A (hydroxyl number ca. 400 - 455 mg KOH/g, catalyst (benzyl methylamine) and blowing agent, stabilizer (N,N,N'N'-tetramethyl hexamethylene diamine). Part B (4500 series) is a polymeric diphenyl-methane diisocyanate (pMDI). APP with an average particle size of 15 µm and an acid value of 1.0 (KOH mg/1g), MEL with a specific surface area of 175 - 225 m^2/g. Sigma Aldrich, Inc, USA supplied APP and MEL. SEP having; average length (44 µm) and Mohs hardness (2 - 2.5) (Lingshou Jiali Minerals Products Company, China). All materials used were as purchased, that is, without treatment.

2.2 Preparation of rigid PU foam composite

Pure RPU foams and IFR-modified RPU foams were synthesized through a box foaming method in the laboratory. All RPUFs were formed in a plastic container. A certain amount of IFR constituents (APP/SEP/MEL), as shown in Table 1, were added into the polyol and the mixture (Part A) was mixed with the support of a mechanical stirrer at 650 rpm for 120 s to obtain a uniform mixture. Subsequently, the pMDI (Part B) was poured into the mixture of part A and each formulation was thoroughly blended at 1300 rpm for the 30 s. The mixture was poured into an aluminium-waxed mould for foam growth to take place in a vertical direction. The newly formed PU foam was conditioned in the mold to cure for 24 hours at room temperature and 50 % relative humidity (Alis et al., 2019). After curing, the foam is cut according to the specimens' standard for testing.

Table 1: The formulations of rigid PU foams used in the study

Samples	Polyol	pMDI	IFR* (phr)
Pure RPUF	50	50	0
RPUF/IFR[a]1	50	50	20
RPUF/IFR[a]2	50	50	16
RPUF/IFR[b]1	50	50	20
RPUF/IFR[b]2	50	50	16

*IFR contains the APP/SEP/MEL blend in a mass ratio: a - 1:2:1; b - 1:1:1. phr – parts per hundred.

2.3 Characterization methods: scanning electron microscopy (SEM)

SEM (Hitachi TM3000 model, Japan) was used to examine pure RPUF and Rigid PU foam/IFR composites morphologies. The innermost surface samples were set by sputter coating before analysis using a tiny layer of platinum and 5kV as the opening voltage was used. The analysis of the results was conducted with Zeiss Ks300 imaging system release 3.0 software.

2.4 Characterization methods: Limiting oxygen index (LOI) test

LOI test was carried out based on ASTM D2863-2013 standard on LOI apparatus (Rheometer Scientific, United Kingdom). The analysis was carried out by preparing five samples from each formulation with dimensions of 100 × 10 × 10 mm^3, length, width, and thickness and average LOI value from each formulation was recorded from the burning of five samples. Polymers with LOI value: above 27 % are (self-quenching), below 21 % are (highly combustible in the air) and between 21 - 27 % are (slow-burning) (Alongi et al., 2015).

2.5 Characterization methods: Underwriters Laboratories (UL-94) test

UL-94 test entails applying a flame to samples in either horizontal or vertical orientation and measuring material reaction after removing the flame (Mohamad et al., 2021). This analysis was conducted in a manually set UL-94 chamber as shown in (Wilkie and Morgan, 2010) based on ASTM D3801. Five samples with sizes of 130 ×13 ×3 mm^3 (length, width and thickness), were prepared. The burning ratings were used to classify the UL-94 test results into HB, V- 0, V-1, or V-2 (Li et al., 2018). HB designated as failed signifying total burning of sample with dripping, V-2 (rapid dripping in fire) and V-0 (no dripping, best grade) (Mohamad et al., 2021).

2.6 Scanning electron microscopy (SEM)

Figure 1a-d depicts the morphology of the pure RPUF and its Composites obtained by SEM for varied IFR formulation (APP/SEP/MEL) of 1:2:1 and 1:1:1and IFR content (20 phr and 16 phr). Figure1a shows that the morphology of pure RPUF is mostly closed-cell, with the high prevalence of closed cells though a small number of broken cells is noticed. The inclusion of IFR caused the reduction of cell size (Figure 1b). The formulation of 1:2:1 shows the most stable structure of RPUF cells with fewer collapsed foam cells (Figure 1 b and c) compared to Figure 1d and Figure 1e. In Figure b and c, more SEP content has been incorporated. The higher dose of SEP in the IFR system elevates the interface between IFR particles and the RPUF matrix. The addition of SEP had raised the viscosity of the RPUF matrix, restricting the collapse and coalesce of the foam cell. This enables better nucleation and cell expansion, inducing the formation of a stable structure for RPUF. Previous studies have found that fire retardant systems containing MEL, silica (Członka et al., 2020), and SEP (Bernardo et al., 2017) can provide more nucleation sites, resulting in more nucleation sites increased cell number and decreased cell size for foam and other polymer matrices.

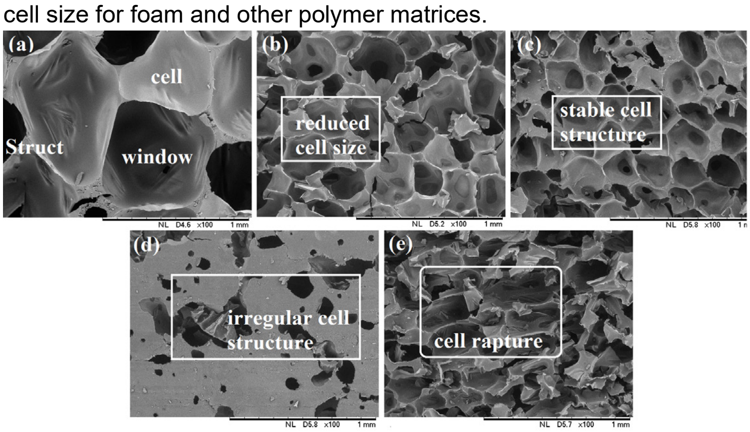

Figure 1: SEM pictures of RPUF at (a) pure RPUF, (b) RPUF/IFRa1, (c) RPUF/IFRa2, (d) RPUF/IFRb1, and (e) RPUF/IFRb2.

2.7 Limiting Oxygen Index (LOI) test

LOI testing was undertaken to examine the flammability of RPUF/IFR composites. Typically, a higher LOI value signifies that more oxygen is needed for combustion i.e., the material is hard to burn. Thus, the fire will retard, which means better flame retardancy of the polymer or material (Shrivastava, 2018). The measurement of LOI values of samples involving a different IFR formulation and number of IFRs aims at exploring the combustion behaviour of RPUF/IFR composites. From Table 2, the composites LOI values is boosted with increasing SEP amount in the IFR system (1:2:1) relative to pure RPUF. In total, the increase was between 21-23 %, with the additions of IFR to RPUF compared to the pristine RPUF. Noticeably, the highest LOI value was achieved for 16 phr IFR (mass ratio 1:2:1), about 23.2 %. In this formulation, it can be noticed that low IFR system loading favours increased LOI value relative to 20 phr, better synergism of the IFR constituents was achieved at 16 phr IFR due to the release of more water vapour at higher SEP content allowing atmospheric oxygen dilution, responsible for their superior LOI value. SEP high specific surface area enables it to boost the dispersal of fillers in a polymer network (Bidsorkhi et al., 2014). The increased LOI value of RPUF/IFR indicates an excellent flame-retardant influence between the APP, SEP, and MEL. Similar result was recorded by Gul et al. (2011), LOI value of composite improved by raising SEP content in their FR system.

Table 2: Limiting Oxygen Index (LOI) of pure RPU foams, and RPUF/IFR Composites

Samples	LOI (%)
Pure RPUF	18.0
RPUF/IFR^{a}1	22.5
RPUF/IFR^{a}2	23.2
RPUF/IFR^{b}1	20.2
RPUF/IFR^{b}2	21.5

*IFR contains the APP/SEP/MEL blend in a mass ratio: a - 1:2:1; b - 1:1:1.

2.8 Underwriters Laboratories (UL-94) test

The UL-94 analysis was conducted to measure RPUF and RPUF/IFR Composites reaction to a withdrawn fire hazard and the time required to self-extinguish. As shown in Figure 3a, pure RPUF almost burns completely, all the way up to the clamp holding the rectangular mold bar relative to the composites (Figure 3b – d). As presented in Table 3, the fire response of the composites is boosted with IFR add-ons compared to pure RPUF. 20 phr and 16 phr IFR at 1:2:1 ratio and 20 phr IFR at 1:1:1 ratio showed the lowest after flame times (t1 plus t2) and achieved V-0 rating relative to pure RPUF failed the UL-94 analysis. A demonstration of inferior flame retardant performance for the pure foam. The results for RPUF/IFR composites confirmed that APP/SEP/MA is a useful IFR formulation for RPUF with a good synergistic effect. As shown in Table 3, RPUF/16 phr IFR (1:2:1) has the best performance in the UL-94 test with 21.4 seconds as the average after-flame time after ignition. The SEP content is ascribed to being twice of APP and MEL in the IFR formulation, offering a robust catalytic surface to support the carbonation response. A study found that the joint action of IFR/SEP further increases the LOI value of polypropylene/IFR and the UL-94 test grade for the composites was upgraded to V-0 from V-1 (de Juan et al., 2019). Also, SEP nanofiller improved LDPE composite flame retardance due to its higher catalytic carbonation potential and high dispersion in the polymer matrix (Li et al., 2019).

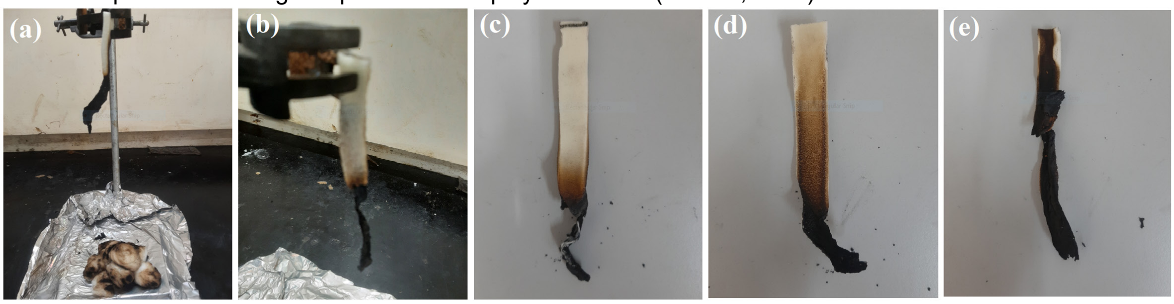

Figure 3: Digital pictures of the UL-94 test for RPUF (a) pure RPUF, (b) RPUF/IFR^{a}1, (c) RPUF/IFR^{a}2, (d) RPUF/IFR^{b}1, and (e) RPUF/IFR^{b}2.

Table 3: Vertical burning test for RPUF and RPUF/IFR composites

Samples	t_1+t_2 (s)	Distance Burned (mm)	V rating	Dripping
Pure RPUF	-	110	Failed	Yes
RPUF/IFR^{a}1	33.2	85	V-0	No
RPUF/IFR^{a}2	21.4	65	V-0	No
RPUF/IFR^{b}1	29.5	70	V-0	No
RPUF/IFR^{b}2	130.2	100	V-2	Yes

3. Conclusions

Rigid PU/IFR composite foams have been effectively prepared from the reaction of polyol and p-MDI with loadings of 20 phr and 16 phr IFR in a varied IFR formulation ratio through the direct mixing method. SEM images showed that incorporating IFRs into RPUF elevated the interface between the IFR particles and the matrix. At lower IFR loading, the foam composites showed a more stable structure. Modification of the RPU foams positively influenced the fire resistance of the composites. From the LOI test results, the fire resistance of the composites at IFR 16 phr (mass ratio: 1:2:1) was greatly improved and the composites excelled in the

UL-94 analysis with a grade V-0, being the best result. An affirmation of improved flame retardancy for the composites relative to pure RPUF.

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