

Effects of Triethyl Phosphate (TEP) and Clay Addition on the Morphological, Compressive Strength and Flame Retardancy of Polyurethane (PU) Foam

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Abstract

Polyurethane (PU) is a polymeric material with great mechanical properties and wide-ranging engineering applications. This material can be tailor made to flexible, rigid or a combination of both depending on the formulation. However, this material is easy to ignite because of its high flammability, releasing a high rate of heat when exposed to a heat source. Thus, research and development to improve the performance of rigid PU always are continuous in industries and the academe. Methods to develop new materials or improve existing techniques are always driven by cost effectiveness and the sustainability of materials used. The addition of a filler to enhance PU mechanical properties and its characteristic is a promising method to meet the objective. In this study, the potential of clay from natural resources originating from ball-clay type was investigated to determine its compatibility within PU foam formulation and its interaction with the conventional nonhalogen base retardant triethyl phosphate (TEP). Samples were prepared in three groups. The first consisted of PU mix with TEP at 3%, 5% and 7% loading; the second group consisted of PU mix with fixed TEP at 3% and clay loading at 3%, 5% and 7%; and the third group had TEP loading set at 5% and clay loading varied at 3%, 5% and 7%. The compressive strength, morphology and flame-retardant properties of PU foams were analysed by scanning electron microscopy, vertical flame test, density test and compressive test.

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1. Introduction

Polyurethane (PU) is a versatile lightweight material that can be tailor-made to wide range of products to fit various applications[1]. This material can be found in numerous engineering products, such as automotive parts, insulation

material, plastic industry, cushioning material, construction material, paint, insulation material, cushioning and coating [2]–[4]. Its unique characteristic permits it to be combined with other materials to produce better composite materials to fulfil specific purpose

of engineering depending on its application. The reaction process of two basic materials, which are isocyanates and polyol, during polymerisation creates repeating and continuous linking structure of urethane groups[2]. Depending on the level of cross linking during polymerisation as a result of different amount compositions of polyol, blowing agent and surfactant determine if the PU forms either into a flexible or a rigid structure. High degree level of cross linking will turn the PU into rigid form of structure with highly closed cell compared with flexible PU which is a result of low level degree of cross linking; more formation of open-cell structure was observed [5]. An application that utilises PU characteristics is insulation material which can be found in construction base material.

PU has been used as a core material for insulation of filling cavity in walls, roofing systems, wall cladding applications, pipe insulation for chillers and floor and wall insulation for space which requires specific thermal control, such as operation theatre in hospitals or server rooms. The production cost is low at bulk quantity, and such materials are easy to produce; PU can be the best option as insulation materials compared with other materials, such as fibrous board, multilayer system or vacuum panel[6]. Closed-cell polymer can act as an insulator barrier to reduce heat transferring within the medium. Another advantages of rigid PU are good dimensional stability, high abrasion resistance, good absorption and rigidity, large surface area and low thermal conductivity[7,8]. Having better strength-to-weight ratio performance characteristic is important for application, such as wall cladding and composite panel insulation application which requires lightweight materials with high strength against environmental effect, such as wind factor.

However, PU-based materials are highly flammable and will easily ignite when exposed to heat source [10]. Their porous structure allows easily air passing and spread the flame efficiently. The interconnected strut joint structure of PU will help the flame spread at a

fast rate and releases high rates of heat due to its petrochemical base composition[9]. With limited oxygen index value between 16–19[10], PU requires a small amount of oxygen to be ignited under heat exposure [12]. Thus, its application is hindered in areas where the level of safety related to fire safety requirement and building codes is mandatory, such as construction material for high-rise buildings [11].

Therefore, continuous research always attracts academic and industry area focus in enhancing the material flammability characteristics and mechanical properties of PU-based materials using sustainability and cost-effective approach. Another method is by adding conventional flame-retardant additives aimed to improve flame retardancy properties. However, usage of other flame retardants, such as halogen-based materials, has been restricted due to being dangerous to human because of releasing toxin gas during combustion process. Some materials, such as magnesium hydroxide, require high amount of loading up to 60%, which will degrade PU mechanical properties. Thus, application of filler is introduced to balance up the mechanical properties and possess better flame retardancy characteristic[12].

2. Materials and Methods

2.1 Materials

The fundamental components for rigid PU foam formulation were polymeric methane diphenyl diisocyanate (PMDI) and polyether polyol with commercial names Orisonate P50 and RG 4620M, respectively. Both were acquired from Oriken Polyurethane Sdn. Bhd (Malaysia). The materials were prepared in ready industrial-grade formulation with polyol supplied with specific blowing agent, catalyst, surfactant and required additives for the complete polymerisation to occur. Triethyl phosphate used for flame-retardant additives from non halogen-based type was purchased from RG Chemicals. Natural clay form ball clay group was obtained from domestic supply from local pottery industry located at Kuala Kangsar, Perak, Malaysia. Silicon glycol copolymer was obtained from KCC Basildon

and used for surface modification process to change the hydrophilic state of the clay.

Table 1 indicates all the materials used to modify rigid PU foam.

Table 1: Material characteristics

Materials	PMDI (Orisonate P50)	Polyol (RG4620M)	Triethyl phosphate (TEP)	Silicon glycol copolymer (SGC)	Ball clay
Properties	NCO content = 30.5 – 32.5 Average functionality = 2.5 – 2.7	Density = 40 ± 2	Mol. weight = 182,15 g/mol	Viscosity at 25°C = 300cS Specific gravity at 25°C = 1.07	Size = 45µm
Characteristics	PU foam basic material		Flame retardant additives	Surfactant for clay surface modification	Reinforcing agent/filler

2.2 Modification of ball clay

Natural clay is known for their hydrophilicity in its pure state and does not have good compatibility with polymer matrix. Surface modification process was conducted to expand the interlayer space of the clay to improve its diffusion level and homogeneity with PU matrix. The pure clay was manually crushed, washed with deionised water and left to dry for hours. The clay particle size must be uniform by controlling the parameter throughout the experiment. To do so, the clay was sieved out using a sieving machine with the last size of <45 µm. The remaining clay was placed in an oven for 12 h with temperature setting of 60 °C. The purpose was to ensure that excess moisture in the clay was removed. A glass beaker was filled with 100ml of deionised water and heated up to 55 °C–58 °C using a magnetic hot plate. Later, 7.6g of silicone glycol polymer was dropped and stirred using a glass stirrer. Acid was dropped accordingly into the solution. The pH level was closely monitored until it reached reading of 1.8 using a pH level metre. In another glass beaker, 400ml of deionised water was heated until reaching the temperature of 55 °C–58 °C, and 5g of sieved clay earlier was poured in. In the next process, the mixtures in the two glass beakers were combined. The mix solution was stirred out for 1 h at 300rpm using a mechanical stirrer. The pH level was maintained at 1.8 throughout the process. The

solution was then left for 12 h at room temperature. Later, the modified clay was filtered out using a filter paper and washed with deionised water to remove any excessive surfactant from the process.

2.3 Preparation of foam

In this study, foam was prepared using free rise direct mixing method. The foam was mixed at a ratio of 1:1.2 for 100g formulation according to manufacturer's specification. However, the total weight was adjusted to 50g of total weight with 1 portion of polyol(22.73g) and 1.2 portion of PMDI (27.27) because it was found to be suitable with the plastic mould used for the foam to grow and form. The foam was produced in three sample groups in total. The first group was prepared only with TEP addition at 3%, 5% and 7% loading. The second group was prepared with addition of clay at 3%, 5% and 7% loading with TEP as fixed parameter set at 3% loading. The third group was prepared similar to the second group with the loading amount of TEP set at 7%. The first step was blending the TEP and clay at various loading with polyol in the first plastic cup. The solution was then stirred slowly at 600rpm for 15 min to ensure it homogeneity. The required polyol was added, and the mixture was stirred at 3000rpm for 20 s. Table 1 indicates all sample names and important parameters used to prepare the samples.

Table 2: Codes and materials composition

Sample	Polyol (g)	PMDI (g)	TEP	Modified Clay
PU/TEP1	22.73	27.27	3%wt = 0.68 g	-
PU/TEP2			5%wt = 1.136 g	-
PU/TEP3			7%wt = 1.59 g	-
PU/TEP1/C1			3%wt = 0.68 g	3%wt = 0.68 g
PU/TEP1/C2				5%wt = 1.13 g
PU/TEP1/C3				7%wt = 1.59 g
PU/TEP2/C1			5%wt = 1.13 g	3%wt = 0.68 g
PU/TEP2/C2				5%wt = 1.13 g
PU/TEP2/C3				7%wt = 1.59 g

2.4 Foam-density tests

ASTMD1622 standard and method were used to investigate the compressive properties of the foam. The foam was cut into samples with a size of 25 mm × 25 mm × 25 mm (length × width × thickness). The accuracy were measured with calliper. The density of the foam were calculated by dividing mass with volume.

2.5 Compression tests

Measurements for compressive test were conducted using Universal Testing Machine Shimadzu with 10 kN load cell. The speed was set at 2.5 mm/min. Deflection rate was set at 10% of the sample height which was 2.7 mm. The foam was cut into cylindrical shape with a size diameter of 27 mm and a height of 27 mm. The foam was cut parallel with foam rise direction. The tests were conducted in accordance with ASTM D1621 compressive test for rigid plastic material. Data of the compressive load and displacement were calculated using computer control software.

2.6 Morphology of foam

Morphology of the foam was analysed using a Quanta 400 scanning electron microscope. Cross section image of the foam was magnified up to 50×, producing a high-resolution image which was used to observe

cell pattern of the foam. Prior to the test, the foam was cut into 1.5cm × 1cm × 0.5cm (length × width × thickness) and coated with thin layer of gold operated at 10kV accelerating voltage.

2.7 Vertical flame test

UL 94 vertical flammability test method was used to gauge the foam performance under heat exposure. Foam was cut into desired dimension (125 mm × 13 mm × 6 mm) and vertically mounted using retort stand. The position of samples was set with a height of 10 mm above from the top burner. A thin layer of cotton was placed 30cm below the mounted samples to capture any dripping of samples from the flame test. The test was initiated by exposing the vertically mount samples with 20 mm height of flame ignite by methane gas. The samples were exposed to heat for the first 10 s and remove from the heat source. Time required for the samples to self-extinguish was recorded as T1. The samples were then exposed back to the heat for another 10 s, and the time required to self-extinguish was recorded again as T2. Any drips of samples at cotton placed below were observed. Samples were categorised in accordance with the criteria as stipulated in Table 3.

Table 3: Criteria for UL specification [13]

Criteria	V0	V1	V2
Total flaming combustion for each specimen	≤10 s	≤30 s	≤30 s
Total flaming combustion for all five specimens of any set	≤50 s	≤250 s	≤250 s
Flaming and glowing combustion for each specimen after second burner flame application	≤30 s	≤60 s	≤60 s
Cotton ignited by flaming drip from any specimen	No	No	No
Glowing of flaming combustion of any specimen to holding clamp	No	No	Yes

3. Results and discussion

Clay modification process is an essential process to enable clay particles become compatible with polymer matrix. The aim is to change the hydrophilic state of the clay to become hydrophobic. In this study, 7.6g of silicon glycol copolymer was used to improve the level of hydrophobic state of the clay, resulting in 58° of contact-angle measurement. Interlayer spacing among clay galleries had become larger and allowed ion exchange process through the surface modification process, which affected the polymer dispersion quality.

3.1 Compression analysis

Table 4 shows the result of compressive test. The data showed the maximum force applied, and maximum values of displacement occurred under the applied force. For samples with the addition of flame-retardant alone, the loading was set at 3%, 5% and 7% with no addition of clay as filler. The maximum amount of force was recorded with sample PU/TEP1 with recorded value of force and displacement of 78.47 N and of 2.15 mm, respectively. Sample PU/TEP3 with 7% loading of TEP was recorded as the second higher value with 70.63 mm with displacement of 1.82 mm. The lowest maximum force applied value was observed with the sample PU/TEP2 with only 67.66 N and 1.83 mm displacement. In general, the value of force applied decreased with TEP addition.

Table 4: Summary results of compression test

Sample code	Flame-retardant additives (TEP) (g)	Amount of SGC for clay modification (g)	Modified clay (g)	Density (g/cm ³)	Max force (N) $\sigma = 15.2$	Max displacement (mm)
PU/TEP1	0.68	-	-	0.039	78.47	2.15
PU/TEP2	1.136	-	-	0.035	67.66	1.83
PU/TEP3	1.59	-	-	0.035	70.63	1.82
PU/TEP1/C1	0.68	7.6	0.68	0.036	82.97	2.02
PU/TEP1/C2			1.136	0.036	78.87	2.10
PU/TEP1/C3			1.59	0.037	77.40	2.25
PU/TEP2/C1	1.136		0.68	0.037	90.47	1.86
PU/TEP2/C2			1.136	0.038	52.42	1.03
PU/TEP2/C3			1.59	0.035	67.19	2.15

As for the second batch of the samples, the addition of TEP was preset at 3% and mixed with clay as a filler at various loading rates (3%, 5% and 7%). The sample with clay loading at 3% recorded a high value of applied force of 82.97 N with displacement of 2.02 mm, followed by sample with addition of clay at 5% with 78.87 N and displacement of 2.10 mm. The sample with 7% loading of clay recorded the lowest amount of force with 77.40 N with 2.25 mm displacement. In general, the value of maximum force applied increased with the addition of clay and slightly decreased at the highest amount of clay at 7%. The sample displacements for all samples were at 0.03 mm/N force applied.

The last batch of sample was mixed with preset 5% loading of TEP mix with various loading rates of clay at 3%, 5% and 7%. From the data, samples mixed with 3% of clay recorded the highest value of force at 90.47 N with 1.86 mm displacement. The second higher value force recorded was with the samples with 7% loading of clay at 67.19 N with 2.15 mm displacement, followed by the sample with addition of clay at 5% at 52.42 N with 1.03 mm displacement.

The addition of TEP and clay generally contributed to the better performance of the PU foam up to certain amount of loading. Increments in maximum force applied were observed compared with the samples with addition of TEP alone. This result may be evidence that the addition of TEP and clay improves the mechanical properties of PU. Quaternary ammonium group found in modified clay may have a catalysing effect during polymerisation, resulting in a better cross-linking reaction. The sample of PU with 5% of TEP loading and 3% of addition of clay showed a high value of compressive strength with only 0.02 mm displacement per applied force. This phenomenon may be due to homogenous mixture achieved by uniform dispersion. The addition of clay helped increase the viscosity value, and the rate of rupture cell consequently occurred at a slow

rate. A similar finding was concluded by Pauziah et al.[14].

Clay may act as a nucleation agent and reinforce filler, but excessively high amounts of filler may cause disruption within the structure. The result of samples with 5% addition of TEP demonstrated significantly decreasing values with 5% loading of clay. The maximum force applied decreased from 90.47 N (sample with 3% clay loading) to 52.42 N clay loading (sample with 5% clay loading). This finding may prove that at the addition of clay more than 3%, no positive synergistic effect exists between TEP and clay, resulting in degradation of performance in mechanical properties. The structure may not be fully exfoliated as caused by the disruption of H-bond connection between clay and polymer matrix. In other research, Chan et al.[15] found that excess filler may result in agglomeration within polymer matrix that can cause clay clustering. Other studies have demonstrated that agglomeration of clay particles within polymer matrix at high loading can interfere hydrogen bonding formation that leads to weakening urethane chemical structure[16].

3.2 Morphological analysis

Morphological analysis was performed by scanning electron microscopy (SEM). The aim was to investigate the relationship between cell formation in terms of sizing, shape, strut and cell window formation upon inclusion of flame-retardant additives and clay as filler. Figure 4 shows images of PU foam cross section with different formulations at the magnification of 50 \times . All samples were constructed from high content of closed-cell structure in rigid foam formation. The core of the cell structure was made from polyhedral shape connected with strut joint, linking other cells in multisided direction and creating a continuous three-dimensional connection.

The compressive test result implied that foam with addition of 5% of TEP mix and 3% of clay recorded the highest value of 8.3.28 N. The SEM image shows that the addition of clay produced more uniform distributions of

cell formation compared with samples only with other formulation. However, the SEM image presents no significant change in foam structure in terms of cell size. As the clay was introduced, the foam cell seemed to be in uniform distribution in general. No significant increment in cell per unit area occurred. Clay can act as a nucleation agent and a reinforce filler if the dispersion level is good[6]. Addition of clay may increase the viscosity of the mixture, lower the expansion ratio and produce thick cell structure. Other findings indicated that addition of filler may help improve foam density by creating small cell size[17] by nucleating concurrently and reducing available gas for bubble to grow, hence resulting in small and dense foam[18–20]. Filler also can be beneficial in terms of enhancing the nucleation by intimate contact between polymer matrix and clay particles through large surface area and fine dimension of added filler [14].

However, the density test result demonstrated that the density of all samples did not show any significantly different value, as listed in Table 5. The homogeneity of PU foam may not have been of good quality given no improvement in density value and change in small cell size. S.Estravis et al. [7] suggested that addition of filler only may improve polymer matrix properties if a strong and good interaction exists among them[7].

With addition of up to 5% of clay, considerable formation of broken cell was noted. This phenomenon may be due to the addition of much clay, as suggested by previous studies that excessive clay can cause agglomeration of clay within the matrix[15,16]. This uneven dispersion of mixture at high amount of filler will result in rupture of cell due to excessive calescence within PU–clay matrix. This scenario will affect the mechanical properties of the foam as can be seen on the lowest result of

compressive test for sample no. 18 with a recorded value of 41.68 N. The possible reason for decreasing performance of foam may be the inference in hydrogen bond connection within PU chemical structure. As a result, this absence of chemical linkage reduced foam mechanical properties, as can be observed with sample PU/TEP2/C2.

3.3 PU flame retardant

An important parameter for material performance investigation is how a material reacts towards heat exposure. As a petrochemical-based material, PU is known for its ease of being flammable. The foam was accordingly tested using a UL 94 vertical flame test. The obtained results of all samples are listed in Table 6. Although the data show variation in results, the flammability classes of V0, V1 and V2 cannot be applied because the samples were completely burn. No flaming drip was observed during the test of all different samples. The samples were tested by batch with incorporation of TEP alone in the composition of 3%, 5% and 7% to investigate the effect inclusion of clay towards flame retardancy properties.

The results indicated that 3% loading of TEP demonstrated the longest time required for the foam to be fully extinguished when exposed to heat source. The test was repeated with TEP loading fixed at 3% and 5% with various compositions of clay at 5% and 7% loading. From the obtained data, incorporation of clay at 3% loading with 3% TEP showed the most positive synergistic effect between flame-retardant additives and clay as filler with 5.9 s required time for foam to self-extinguish. However, the result implied that the time required was shorter in comparison with PU filled with TEP alone. This result may be caused by the uneven dispersion level of the clay, and filler distribution was not dispersed evenly within the matrix.

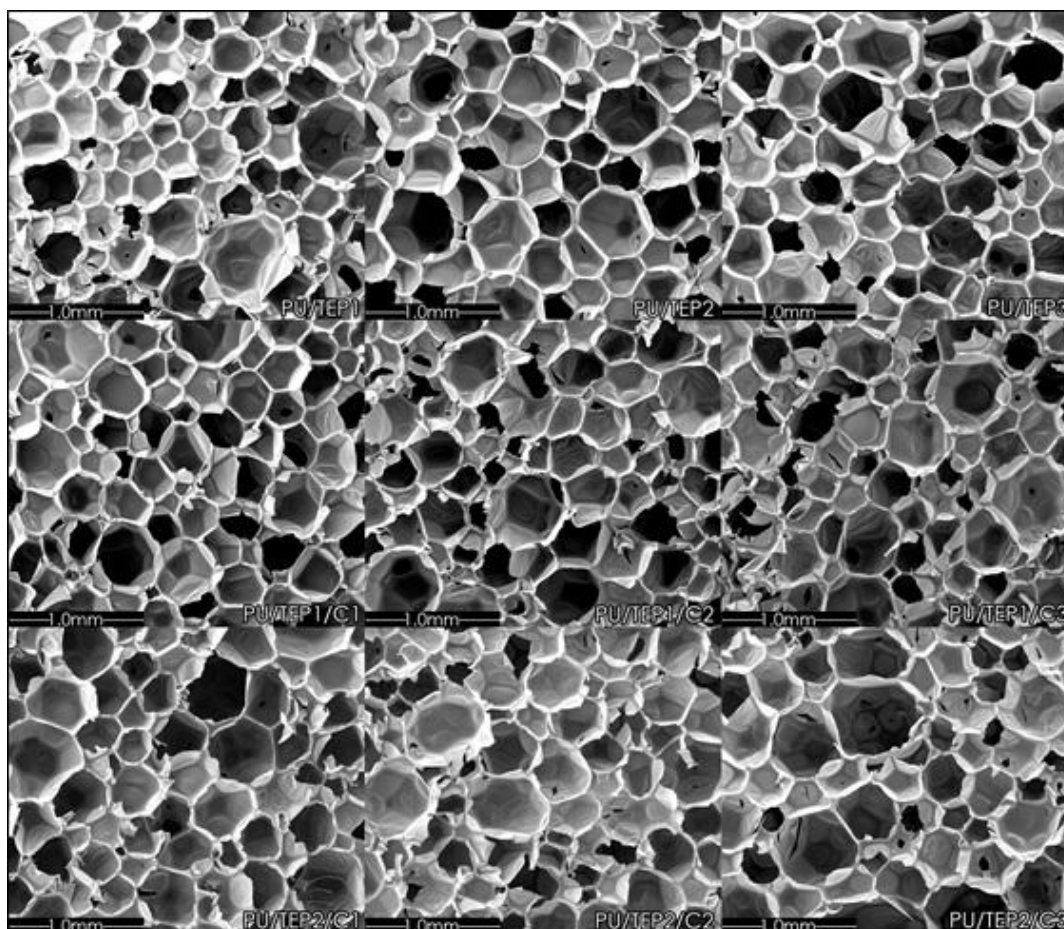


Figure 4: SEM image of foam at different compositions a50× magnification

Table 6: Results of PU vertical flame test

Samples	After flame T1 (s)		
	Minimum	Maximum	Average
PU/TEP1	3.13	9.46	6.07
PU/TEP2	4.48	6.46	5.23
PU/TEP3	3.23	8.46	5.7
PU/TEP1/C1	4.63	8.68	5.9
PU/TEP1/C2	2.25	5.23	3.35
PU/TEP1/C3	2.50	3.55	4.92
PU/TEP2/C1	2.95	5.60	4.22
PU/TEP2/C2	4.23	7.29	5.51
PU/TEP2/C3	3.65	5.78	4.76

4. Conclusion

The aim of this study was to investigate the potential PU foam from natural ball clay as a filler to enhance the efficiency of flame retardants assisted with other mechanical properties. The density test indicated that inclusion sample with TEP alone and

combination of TEP and clay did not affect the density of the PU foam. The compressive test results showed that incorporation of clay did not affect the result of the compression strength of the material. With addition of 3% clay, samples at different TEP composition recorded the highest value compared with

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