COMPRESSION STRENGTH, HEAT DEGRADATION AND UL-94 FLAMMABILITY PROPERTIES OF POLYURETHANE FILLED BENTONITE COMPOSITE FOAMS

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ABSTRACT: This study has reported the potential of bentonite mineral clay as filler, to improve the resulted properties of polyurethane (PU) based composite foams. Bentonite was incorporated into PU formulation, through high-speed mechanical stirring process and has been reacted at 1:1.4 ratio of polyols and isocyanate. The effects of bentonite addition at various loadings (0 – 5.00 wt. %) has been evaluated in-terms of their compression strength and fracture toughness behavior, the fracture morphology, heat degradation and UL-94 flammability properties. From this work, it was found that, at lower addition of bentonite filler (0.50 wt. %), the compression strength had improved about 77%, while heat degradation characteristic of PU/bentonite composite was significantly enhanced at higher bentonite loading. It was also proven that the added bentonite mineral clay filler is actually able to retard the fire, due to their extinguishing characteristics. Hence, related flammability mechanism of PU/bentonite composite foams has been suggested. Addition of bentonite mineral clay filler into PU gives benefits to the mechanical strength, heat and flammability properties of PU/bentonite composite foams, at different filler loadings variation. This, would solve several issues related to lower mechanical strength, limited fire behavior and worst heat resistance characteristics of unfilled PU foam system.

1.0   INTRODUCTION

Nowadays, polyurethane (PU) have been utilized in wide range of applications. For instance, as adhesive, foam and coating purpose. PU based product are performed their function in many service environments. However, PU materials are suffered with lack resistance at higher temperature. Early degradation and structural failure may limit their versatility when utilized at an elevated temperature. By incorporating PU foam with certain filler types, would enhance the resulted properties of PU based composites foams [1].

Past study, has found that, addition of carbon nanotubes (CNTs) into PU delays the thermal degradation, increase stability and flammability attributes of PU/CNTs composite foams. On the event of fire, formation of carbon layer by CNTs had extinguished it [2]. In addition, for PU filled wood flour (WF), the mechanical strength and fire behavior are improved with increasing WF content [3].

Related past study, utilizing mineral clay as filler, found that it has acted as pores nucleation agent, that reducing the rate of pore growth, which destructing the foam cell size [4]. This condition has created higher content of small pore size, with small mean average of closed cell composite foams. Closed pore structure is highly intended for good thermal insulation effects, as it has provided an air gap that dissipate the heat during the event of heat exposure [5].

Reduction of cell size, caused smaller radiation that reducing the thermal conductivity of foams [6]. In rigid polymer foam, large amount of phase interface has led into more scattering and decrease radiation heat flux. Small size of cell pores creates comparable mean free path of gas molecule that led into reduced heat conductivity [7]. Another opposite example, addition of flax fiber into PU foam has increased the apparent density but worsen the heat insulation behavior of produced PU/flax fiber composite foams [8].

Addition of mineral clay could have resolved the thermal stability issue of PU based composite foams. In the event of heat exposure, the foam experienced heat degradation which collapsing the mechanical and physical structural integrity of the foam. Presence of mineral clay would be acted as anti-fire agent to stop the propagation. However,

due to higher density of mineral clay, it tends to precipitate during the foaming stage. This condition limits the dispersion of mineral clay filler that hamper the overall performance of PU/mineral clay composite foams. Hence, it was very critical to determine the optimum filler loading to be added into the PU foam system, for the maximum resulted properties.

This study was carried out to prepare and to characterize the PU based composite foams filled bentonite mineral clay. The effects of bentonite loadings were evaluated to enhance the resulted compression strength, fracture toughness, heat resistance and flammability properties of PU/bentonite composite foams. Bentonite are selected since it has the characteristic of anti-flammable, higher resistance toward heat and are absolutely cheap. Hence, the effects of bentonite mineral clay filler loadings toward improving the mechanical, thermal and flammability properties of PU/bentonite composite foams, were evaluated further in this work.

2.0   METHODOLOGY

2.1   Materials and Foaming Procedure

There are three important raw materials involved in this study, which are bentonite mineral clay, palm oil based polyols and methylene diphenyl di-isocyanate (MDI). As supplied bentonite was unmodified from mineral rock, that composed of 70% silicone oxide with dominant presence of quartz and cristobalite than the montmorillonite, and having about 15% of moisture content. This clay possessed light gray color, pH about 8.1 - 10.5, specific gravity of 2.50 g/cc, bulk density of 1.18 g/cc and melting point at 1200°C.

Palm oil based polyols (R3310) were purchased from Polygreen Chemical (Malaysia) Sdn. Bhd. This polyol possessed 2.0 of Gardner number, 92 – 98 mg KOH/g of hydroxyl number, about 2000 – 2500 mPa.s at 25°C of viscosity, pH of 6.5 – 7.5, acid value of < 2.0 mg KOH/g, < 0.15% of water content and about 2% of calculated functionality.

Isocyanate used is an analytical standard of MDI type. MDI used is colorless with pungent smell. MDI possessed 314°C of boiling point, 40°C of melting point, density of 1.18 g/ml at 25°C and stored at normal room temperature. PU/bentonite composite foams were prepared through free rise foaming method. Bentonite clay powder was first dried in a drying oven at 60°C for two hours to eliminate the moisture.

High speed mechanical stirring process was applied to disperse bentonite filler within R3310 polyols solution. Bentonite filler loadings are varied into 0, 0.50, 0.75, 1.00, 3.00 and 5.00 wt. % of filler addition. High speed stirring process was performed at 30 minutes of mixing period and 1000 rpm of mixing speed. Later, after the mixing, the MDI isocyanate was added for foaming procedure at 1:1.4 of polyols and isocyanate mixing ratio. The mixture has been manually hand-stirred for about 30 seconds. The mixture of polyols/bentonite and isocyanate was poured into mold for free rise foaming mechanism.

2.2   Mechanical Properties Testing

There are two types of mechanical testing performed in this study, which are compression and fracture toughness testing. The standard used for compression and fracture toughness are ASTM D1621 and ASTM D5045, respectively. The compression strength was determined at parallel direction of foam rising. The compression and fracture toughness tests were performed at standard control room temperature by using the 50 kN Universal Testing Machine (UTM) model Shimadzhu, from Japan. The crosshead speed used are 20 mm/mins at 50% of compression limits. For fracture toughness testing, it was performed at a span length of 80 mm at 2 mm/min of crosshead speed. For both tests, about seven samples were tested for each PU/bentonite formulation for an averaging purposes.

2.3   Heat Degradation and UL-94 Flammability Testing

Heat degradation of PU/bentonite composite foams was evaluated by the thermogravimetric (TGA) test. TGA was performed by using Perkin Elmer TGA testing machine. The sample was heated up to 600°C from room temperature, at a heating rate of 20°C/min, in a nitrogen atmospheric condition.

The UL-94 flammability test was carried out in accordance to ASTM D635. The PU/bentonite composite foams were cut into 125 mm x 13 m x 3 mm of dimensions. At least about three specimens were prepared for each PU/bentonite composite formulation. For UL-94 flammability testing, the relative linear rate of burning and the extent of burning time were determined. The composite foam sample was scribed with mark at 100 mm at one end for burning rate calculation and then horizontally mounted with flame applied at 45° inclined of the sample.

The tested sample was exposed with gas flame for 30 seconds. The time and extent of burning are measured and rated on the basis of mean

values from three measurements, which refer as the following scheme:

HB 1 = Burning rate between marks ≤ 38 mm/min
HB 2 = Burning rate between marks ≤ 76 mm/min
HB 3 = Extinguished at prior of 102 mm marks

2.4   Foam Morphologies via Scanning Electron Microscope (SEM)

The fracture surface of PU/bentonite composite foams was cut and mounted on the aluminum stub for coating with thin layer of gold palladium, to avoid the electrostatic charging. The observation was performed at the average accelerating voltage of 40 kV by using the scanning electron machine model Leo Evo, by Zeiss, UK. The magnification power used for observation was standardized into 20x of magnification power. The PU/bentonite composite foams properties was further inter-correlated with the foams morphologies.

3.0   RESULTS AND DISCUSSION

3.1   Compression Strength of PU/bentonite Composite Foams

The effect of bentonite filler loading into compression strength of PU/bentonite composite foams was depicted as in the following Figure 1. It was found that, addition of low loading of bentonite filler at 0.50 wt. % has drastically increased the compression strength at about 77% of positive improvement than unfilled PU foam. An increase in compressive strength can be partially explained on the basis of strong interaction between bentonite filler and the PU foam matrix, due to good dispersion of bentonite at low filler addition. The ability of bentonite filler to nucleate the pores formation at low loading was due to better dispersion of bentonite in the composite foams [9].

However, increasing the bentonite filler content shows the decrease pattern of compression strength. At 5.00 wt. % of bentonite loadings, shows major decreasing pattern, from 0.283 MPa to 0.158 MPa which was around 44% of reduction than PU filled 0.50 wt. % of bentonite. At higher filler loading, the cumulative surface area of bentonite particles filler has promoted the agglomeration, due to increase surface energy between them. Besides, it had decreased the PU pore cell size. Bentonite mineral clay as nucleation agent for gas bubbles formation had lost their function due to increase viscosity of polyols/bentonite mixture at higher bentonite loading, which obstructed the foaming process. Also, at higher bentonite loading, the filler has the tendency to tear the wall

of PU foam cellular structure, which obstruct the PU/bentonite composite strength, during the compression event.
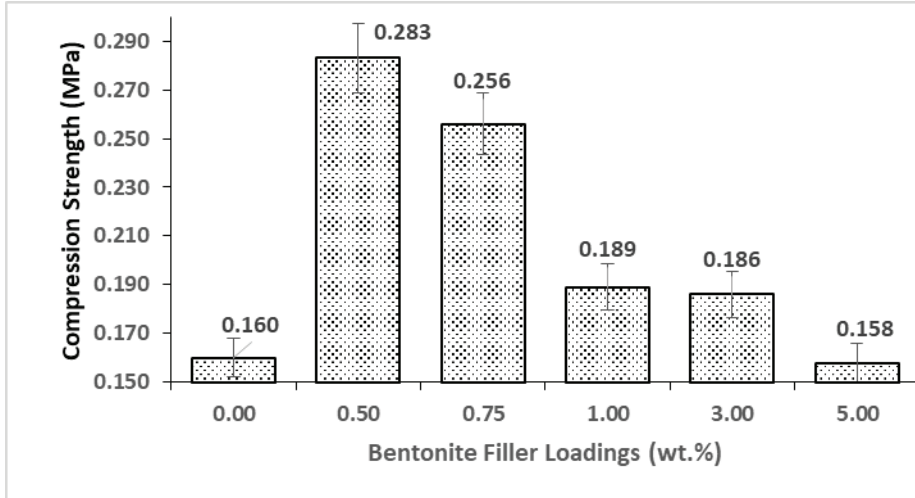

Figure 1: Compression strength of PU/bentonite composite foams

3.2   Fracture Toughness of PU/bentonite Composite Foams

The fracture toughness results were plotted against bentonite filler loadings, as depicted in Figure 2. It was clearly found that, the increasing trend of fracture toughness value are in parallel with bentonite filler loading up to 1.00 wt. % addition, before experiencing the decrease trend at higher filler loadings. The properties enhancement only optimum at certain value of filler addition [8-9].

At positive improvement of fracture toughness behavior, addition of bentonite filler was acted as nucleation sites that promotes the formation of closed pores structure, which contributed to improving the fracture toughness properties. Closed pores structure has responsible to delay the crack propagation in the event of applied load. About 120% of improvement was experienced by PU/bentonite composite foam at 1.00 wt. % of filler loading than unfilled PU foam. At this point, presence of bentonite had strengthened the cell struts as formation of more closed pores was able to enhance the fracture toughness. However, at one point, the fracture toughness performance has started to descend when the filler loading was increased after 1.00 wt. % of bentonite addition.
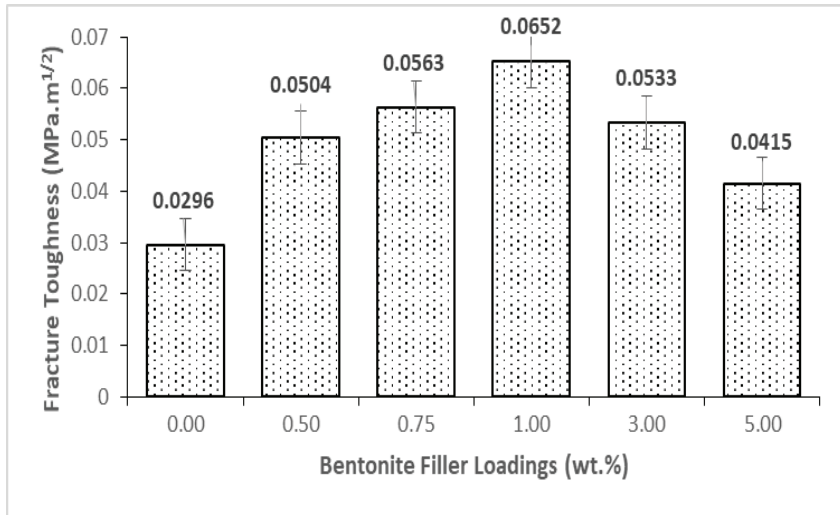
Figure 2: Fracture toughness of PU/bentonite composite foams

At 3.00 wt. % of bentonite loading, the fracture toughness had decreased about 36%. Based on morphological observation, the decreasing pattern was responsible by an inhomogeneous cell formation that promotes the pre-mature cell rupture during the applied load and fracture event. In addition, at 5.00 wt. % of bentonite loading, it had caused the cell rupture due to worst agglomeration of bentonite filler. Presence of agglomeration sites has acted as weakening point for premature failure, that lowering down the fracture toughness.

3.3 Heat Degradation of PU/bentonite Composite Foams

Thermogravimetric (TGA) analysis is used to evaluate the thermal stability and heat degradation behavior of PU/bentonite composite foams. The effects of bentonite filler loadings were evaluated based on three selected thermogram which are PU/bentonite composite foams samples with 0 wt. % (as control sample), 0.50 wt. % (low filler loading) and 5.00 wt. % (high filler loading). The overlaid thermogram were depicted as in Figure 3. From the thermogram, it was found that, typically the PU/bentonite and unfilled PU samples was started to decompose at 300°C and are completely degraded at about 450°C with left residue. Presence of bentonite in PU/bentonite composite foams had tremendously enhanced the thermal stability. Addition of 5.00 wt. % of bentonite shows the highest heat stability performance with about 85% of left residue after the thermal event. Enhanced thermal stability has contributed by added bentonite which possessed higher thermal resistance character of ceramic mineral clay materials.

Addition of bentonite has enabled the PU/bentonite composite foams to sustain the foam molecular rigidity toward chemical reaction, that lead into degradation, which limits the macromolecular chain excitation and motion gained by the thermal energy, during exposure of heat [10]. Referring to the thermal event, basically there are two identical degradation steps experienced by all the tested samples. First degradation step due to the collapse of PU structure that was experienced at temperature up to 300°C. Later after that, the second degradation step was started at 350°C onwards, which mainly dominated by the degradation of bentonite filler. The higher the filler content, the shorter the fall curve until the formation of stable plateau, which indicates the degradation end. On ranking basis, PU/bentonite composite foams with 5.00 wt. % bentonite addition had left about 85% of residue, followed by 79% and 65% of left residue for 0.50 wt. % and unfilled PU sample, respectively.
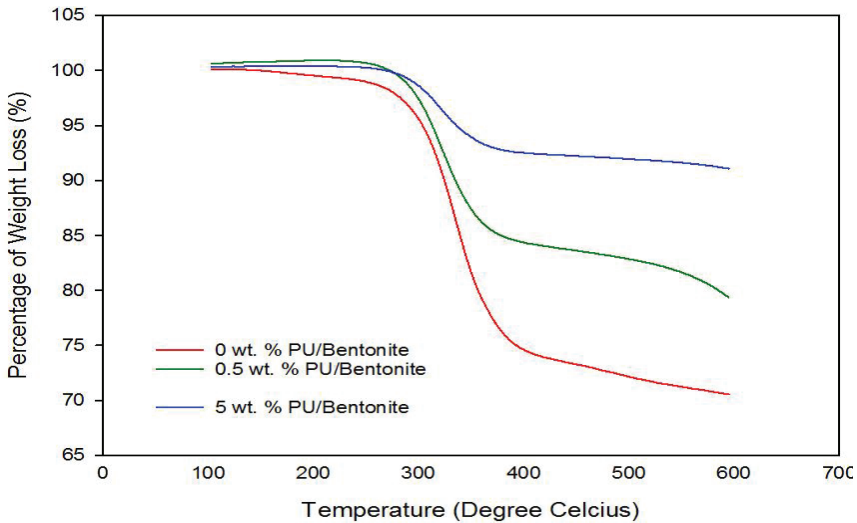

Figure 3: Heat degradation thermogram of PU/bentonite composite foams

3.4 UL-94 Flammability of PU/bentonite Composite Foams

The flammability test was conducted to assess self-extinguishing fire behavior of PU/bentonite composite foams. Figure 4 shows after the test burnt condition for every tested sample. It shows that the only PU/bentonite composite foam that survived the fire test was possessed by the sample with 1.00 wt. % of filler addition. The PU/bentonite at 1.00 wt. % of filler loading does not experienced fully burnt condition. During the test, it was observed that there is no dripping formation of burnt composite foams for all the tested samples after 30 seconds of burning period. The entire samples had extinguished prior of 102 mm

scribed mark. Thus, it can be categorized as HB3 where extinguishment occurred at before 102 mm of scribed mark.

Although the thermogravimetric results had shown the foams with higher bentonite content at 5.00 wt. % had possessed the higher heat stability, but the flammability test has evidenced that was not the case. UL-94 flammability test result was in parallel with the fracture toughness finding, where the factor of bentonite filler dispersion played a major role in safe-guarding the composite foam sample for better fire resistance. Low filler loading sample had burnt at the fastest rate as compared than PU/bentonite composites at higher filler loading, starting at 1.00 wt. % into 5.00 wt. %. The unfilled PU foam had experienced complete burning. It shows that the filler loading plays a promising role in extending the burning time. To explain this situation, it can be related with the role of bentonite mineral clay which behaving as refractory material that able to resist the fire.

Self-extinguishing behavior of the tested sample can be explained by the mechanism of solid carbon destruction at the disperse state, assuming the bentonite would behave in a similar manner during the fire exposure. The formation of hydroxyl radical had oxidized the solid carbon via decomposition into hydrogen or water vapor. The presence of oxides, carbonates or hydroxides will significantly reduce the decomposition. In addition, a reaction with metal oxides in which carbon is directly oxidized or intermediates of soot are neutralized by contact with metal species [11]. The following section has summarized the proposed mechanism for destruction of solid carbon at the dispersed phase. From the reaction scheme as shown in Equations (1)-(5), M could be substituted with any mineral type elements like Si, Al, Ca or KAlSi.
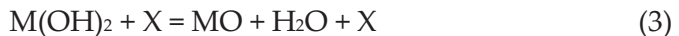
$$MO + H_2 = MOH + H\bullet \qquad (1)$$
$$MOH + H_2O = M(OH)_2 + H\bullet \qquad (2)$$
$$M(OH)_2 + X = MO + H_2O + X \qquad (3)$$
$$H\bullet + H_2O = \bullet OH + H_2 \qquad (4)$$
$$\bullet OH + C_{(s)} = CO + H\bullet \qquad (5)$$

Figure 4: Burnt samples after UL-94 flame retardant test of PU/bentonite composite foams

3.5 Foam Morphologies of PU/bentonite Composite Foams

Three different samples were selected for fracture surface morphologies observation of PU/bentonite composite foams. The control sample of unfilled PU foam, the worst and the best PU/bentonite composite foams were taken from the fracture toughness test. The observation was made at 20x of magnification power. Figure 5 shows the cross sectional view of fractured samples that depicts the morphological view of closed pores, open pores and the cell rupture. For comparison purposes, unfilled foam sample and PU/bentonite composite foams with 1.00 wt. % and 5.00 wt. % were observed.

Sample with 1.00 wt. % of bentonite addition was selected as it possessed the best fracture toughness performance. It was found that, from Figure 5(b), this sample shows better bentonite filler dispersion that promotes the formation of smaller pores or cell sizes, which contributing towards enhancing the overall surface area, benefited for fracture toughness performance. Enhanced surface area of cell walls and struts could help to prolong the propagation of crack, during the fracture event. In addition, well dispersed bentonite filler also able to act as stopper for crack propagation. Due to this, it was also clearly detected that there is less presence of cell rupture throughout the tested sample. This situation has supporting the role of bentonite filler at 1.00 wt. % of filler addition in enhancing the toughness of produced PU/bentonite composite foam. Meanwhile, this is not the case for PU/bentonite composite foam with 5.00 wt. % of filler addition. For this sample, worst bentonite filler agglomeration was detected at several foam spots.
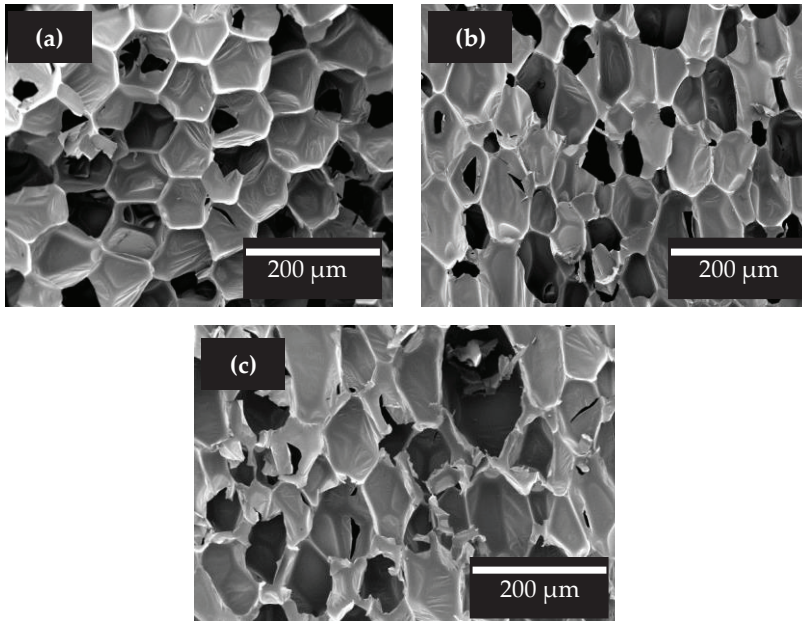
Figure 5: SEM images at 20x of magnification for (a) unfilled PU foam, (b) PU/bentonite composite foam with 1.00 wt. % and (c) PU/bentonite composite foam with 5.00 wt. %

Worst dispersion of bentonite had caused the formation of weakness points at the agglomeration sites, which are responsible for pre-mature crack during the fracture event. Also, at the highest filler loading, it was found that inhomogeneous formation of cells shape and size are due to bentonite agglomeration [12]. Too much filler loading had caused the cell rupture and retard the formation of homogenous closed cells. Poor dispersion of bentonite filler loading had diminished the overall performances of produced PU/bentonite composites foams. Homogeneous dispersion of filler and strong interfacial interaction with matrix is required for some excellence composite properties [13].

4.0   CONCLUSION

In overall, it was found that, addition of bentonite mineral clay filler is able to improve the resulted end properties of PU/bentonite composites foams. However, this only applies up to certain level of filler weight percentage. The factor of homogeneous dispersion of bentonite filler within the PU foam matrix has greatly influenced the mechanical and flammability properties of composites. Good filler dispersion had influence the nucleation of closed pores formation which beneficial to increase the fracture toughness and compression strength, as well as

the flammability behavior. In addition, it also produced homogenous shape of cell pores and struts, and provide collapse resistance of PU foams, as evidenced by PU/bentonite composite foam at 1.00 wt. % of bentonite loading. Worst filler dispersion of PU/bentonite composite foam at 5.00 wt. %, had diminished the entire properties except for thermal stability. The nature of high heat stability of bentonite, gives advantage of stable heat degradation to PU/bentonite composite foam. Hence, the effects of bentonite filler loading are highly significant in influencing the mechanical, heat resistance and flammability properties of PU/bentonite composite foams. As for future work recommendation, it is best to investigate the effect of surface treatment into bentonite mineral filler for better enhancement of PU/bentonite composite foam properties.

ACKNOWLEDGMENTS

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