

Development of Rigid Bio-Nanocomposite Polyurethane Foam for Load Bearing Application: Effect of Surfactant Composition

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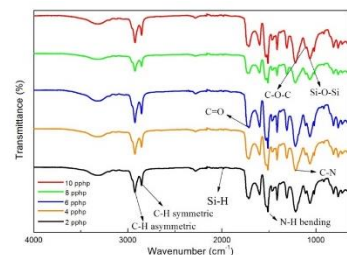
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Graphical abstract



Abstract

This paper presents the preliminary work on rigid palm oil-based polyurethane foam reinforced with nanoclay for load bearing purposes. In this work, palm oil-based polyol (POP) was reacted with polymeric 4,4'-diphenylmethane diisocyanate (p-MDI) along with distilled water as the blowing agent, silicone surfactant, and montmorillonite (MMT) clay as filler to produce rigid bio-nanocomposite PU foam. The produced foams are varied by the amount of surfactant used in every foam formulation. The foams are characterized for their morphology and compression strength. The cells inside the bio-nanocomposite foams are indicated to be closed cells. No apparent changes in cell size at higher surfactant content. The compression strengths shows gradual decrease as the surfactant composition increases, while gradual increase in density is observed when nanoclay content is increased, but up to 6 wt. % only. All in all, as indicated by this preliminary finding, rigid palm oil-based nanocomposite PU foam is a promising alternative for its conventional petroleum-based counterpart.

Keywords: Polyurethane foam; palm oil; surfactant; mechanical properties

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1.0 INTRODUCTION

It is not uncommon for polymeric composite foams to be used in industries. Due to their excellent thermal and mechanical properties, polymeric foams like polyurethane (PU), polyvinylchloride (PVC), and polystyrene (PS) with their different chemical reactions are widely applied in many field of industries, such as insulation, acoustic damper, bedding, coating, and furniture; up to even in aircraft and automotive parts [1-4]. Among the many types of polymeric foam, PU emerges as the most commonly and widely used. They account for the largest global market at approximately 53% [5], which makes them the most widely used polymeric foam with the production of rigid PU foam alone is 23% of the total [6]. Polyurethane foams; like any other polymeric foam however, consumes petrochemical feedstock in their production. With the recently decreasing petroleum supply and environmental issue, numerous works were carried out to obtain an alternative for the petrochemical components of the foam production from bio-renewable resources. It is proven from past researches that many vegetable oils like rapeseed oil, palm oil, canola oil, and soybean oil can be modified and used to react with isocyanate to produce PU foam [1-4, 6-8]. However, due to its abundance in supply and low cost in South East Asian countries like Malaysia and Thailand, palm oils have garnered much attention for research. All the mentioned vegetable oils except

castor oil need to be modified to introduce hydroxyl groups, and this can be done by methods including transesterification, epoxidization, or ozonolysis followed by hydrogenation [2].

Many studies to date were carried out utilizing palm oil-based polyol in the production of PU foam [4, 9-11]. Their findings indicate that replacement of petrochemical-based polyol with that of palm oil-based either partly or completely enhances the mechanical and thermal properties of the produced foams as compared to the petrochemical-based foams. To further enhance the mechanical and thermal properties of the bio-composite PU foams, nanoclays are introduced into the foam. Montmorillonite (MMT) is the most commonly used clay mineral. Several studies reported incorporating MMT nanoclay as fillers in PU foam matrix and the findings indicate MMT nanoclay enhances mechanical properties and thermal stability of the foam [1, 12].

Another key material in the production of PU foam is surfactant, which is used to help stabilize the foam structure by thinning of the cell walls and stabilizing the cell windows. It also promotes nucleation of carbon dioxide CO₂ gas from the isocyanate-polyol reaction, and also contributes to make the raw materials with different polarities compatible; hence forming homogenous mixture [13]. Absence or insufficient of surfactant amount often leads to coalescence and collapse of foam [13, 14]; while excess in amount acts as plasticizer, leading to over-stabilized cell in foam and deterioration in properties [15]. The

most commonly used surfactant is silicon surfactant such as polydimethylsiloxane (PDMS). A study conducted by Zhang *et al.* [13] indicated that smaller cell size was achieved as a result of increasing silicone/polyether ratio as this lowers the surface tension of the foaming system.

Since the properties of PU foams are governed by the polyol, surfactant, and blowing agent [16], it is essential to study the

significance of each component in influencing the end properties of the foam. This paper presents preliminary work on development of green rigid PU nanocomposite foam for load bearing applications such as in aeronautical industry. Foams of different surfactant content are fabricated in closed mold, and characterized for their density, morphology and compression strength.

Table 1 Foam formulation for PU bio-nanocomposite with various surfactant composition

| Sample Code | NCO:OH ratio | p-MDI (g) | Polyol (g) | Distilled Water (pphp) | MMT (wt. %) | Surfactant (pphp) |
|-------------|--------------|-----------|------------|------------------------|-------------|-------------------|
| P1 | 1:1 | 50 | 50 | 1 | 4 | 1 |
| P2 | 1:1 | 50 | 50 | 1 | 4 | 2 |
| P3 | 1:1 | 50 | 50 | 1 | 4 | 3 |
| P4 | 1:1 | 50 | 50 | 1 | 4 | 4 |
| P5 | 1:1 | 50 | 50 | 1 | 4 | 5 |

2.0 EXPERIMENTAL

2.1 Materials

The raw materials used in this study include palm oil-based polyols; polymeric diphenylmethane-4,4'-diisocyanate (p-MDI); silicone surfactant Tegostab B-8404, K10 MMT nanoclay, and distilled water. All materials are used as obtained without further modification.

2.2 Preparation of Foam

The palm oil-based polyol was first weighed according to desired formulation as illustrated in Table 1 together with silicone surfactant and distilled water before stirred for 2 minutes with magnetic stirrer at 500 rpm for homogeneity. The powdered modified MMT was then introduced into the solution and further stirred for 2 minutes, forming premixture. *p*-MDI is weighed according to desired formulation and reacted with premixture, stirred for 45 seconds at 500 rpm before transferred into closed mold of dimension 100 x 200 x 30 mm³ for self-rising. The foam is conditioned at room temperature for 24 hours before demolded, and undergoes the same condition for another 24 hours before cut into specimen and undergoes testing.

2.3 Fourier Transform Infrared (FTIR) Spectroscopy

Fourier-transform infrared (FTIR) spectroscopy analyzer Perkin-Elmer Frontier was used to carry out infrared spectroscopic measurements of the PU nanocomposite foams. Sample foams were scrapped into powder form and pressed against ATR crystal for total contact with force gauge maintained at value of 80. Infrared spectroscopy was carried out within the range of 4000-650 cm⁻¹ at a resolution of 4cm⁻¹ with a total of 16 scans were taken.

2.4 Optical Microscopy

Optical microscopy is conducted to study the microstructure of the produced foam. The PU nanocomposite foams were cut into thin films and viewed under Olympus 71 inverted microscope.

2.5 Density of Foam

Foam sample density was determined using the standard ASTM D1622. Samples were cut into cubes of size 50 x 50 x 30 mm³ using bench saw prior to being weighed using digital balance.

Dimensions of the samples were measured using digital vernier caliper. Average of at least five samples was taken into consideration.

2.6 Compressive Properties

Compression test was carried out following the standard ASTM D1261. The foams were cut into cubic sample sizes of 50 x 50 x 30 mm³ prior to be tested using the Universal Testing Machine Instron Series 5408 with crosshead speed of 5mm/min. Data of compressive load and displacement were sampled via test machine's computer control software at a rate of 10 points per second. Compressive strength was determined following procedure A (absence of yield point, stress taken at 10% deformation). An average of five samples was taken and reported.

3.0 RESULTS AND DISCUSSION

3.1 Fourier Transform Infrared (FTIR) Spectroscopy

Figure 1 illustrates the infrared spectroscopy of the PU nanocomposite foams varying the surfactant compositions. All in all, the spectra exhibits the typical pattern for the formation of PU foams; which are the formation of urethane linkages N-H, C-N, and C=O at bands 1510, 1216, 1713 cm⁻¹; respectively.

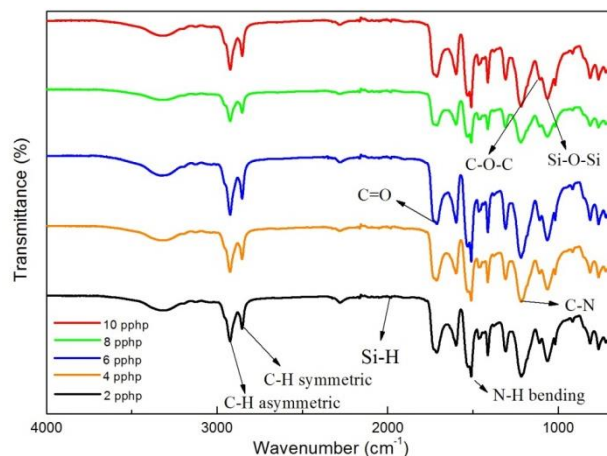


Figure 1 Infrared spectra of PU nanocomposite foams with various surfactant composition

With reference to the spectra, the bands at 2926 and 2848 cm^{-1} were attributed to the C-H symmetric and asymmetric stretching vibration of PU foam and polyether chains attached to the main polysiloxane chain, respectively. The absorption bands at 1065 cm^{-1} , 1110 cm^{-1} , and 1983 cm^{-1} were corresponded to Si-O-Si, C-O-C and Si-H functional groups of polysiloxane backbone. Successful inclusion of silicon surfactant into PU foam may be attributed for the intensity of band Si-O-Si. As can be seen, the intensity of this band for 8.0 pphp surfactant content is the lowest, suggesting that the surfactant may not fully be included inside the PU foam. However, as will be discussed in latter parts of this paper, the low intensity of the spectrum may be attributed to the non-homogenous distribution of the silicon surfactant inside the PU foam as the foams with 8.0 pphp surfactant compositions produces the largest standard deviation for compressive strength data. Large standard deviation suggests non-uniformity of the density distribution within the PU foam, which may be contributed from the non-homogenous distribution of silicon surfactant. This finding also suggest that the increase in surfactant content does not alter or affect the overall reaction rate [13] as the intensity of bands for excess hydroxyl, OH groups at 3320 cm^{-1} and excess isocyanates, NCO groups at 2279 cm^{-1} remained unchanged. No observable change can also be seen for the main PU linkages' bands as the surfactant content changes.

Apart from spectrum for 8.0 pphp surfactant, it can actually be observed that spectra 6.0 to 10.0 pphp surfactants portray almost identical pattern, suggesting that at higher surfactant composition, the surfactant may no longer influence the morphology of the PU foam. This will be proven later on from the data of compression strength and optical microscopy.

3.2 Optical Microscopy

From the optical microscopy conducted on the foams, it can be observed the decrease in cell size and increase of cell density of the foams. This is attributed to the surfactant which, as mentioned earlier, functions as to promote nucleation of CO_2 gas from the isocyanate-polyol reaction [13]. Zhang *et al.* [13] and Han *et al.* [14] stated that the silicone surfactant is able to lower the surface tension between the cells and hence, prevent coalescence. This in turn contributes to the forming of smaller and more uniformed cells. However; at higher surfactant composition (> 4.0 pphp), it is observed that no distinct changes in the cell sizes can be detected, suggesting that the surfactants no longer contribute in stabilizing the cell foam. Han *et al.* however predicted an increase in cell size at higher surfactant content due to self-aggression of surfactant-polymer reaction; which in turn lowers the surface tension and increase the pressure inside the bubbles [14]. Even though the increase in cell size is not detected, the deterioration of properties can be clearly observed, which will be discussed later. Another factor believed to contribute to the rapid decrease in cell size is the dispersion of the MMT nanoclay into the PU matrix. Many previous works have proven nanoclay to act as bubble nucleating agent, resulting in reduced cell size [1, 15-17]. However, the amount of 4 wt. % nanoclay used in this research might already have effect on the foams cell structure. As nanoclay can also reduce the cell size of the PU foam, it is believed that the amount of nanoclay utilized in this study might have already maximized the cell size reduction. This is because from the finding of this study, the cell size-reduction effect by the surfactant is believed to have reached its peak somewhere circa 2.0 pphp. The effect is manifested in its compressive strength, which will be discussed in latter part of this paper.

3.3 Foam Density

The result for the density of the palm oil-based nanocomposite PU foam is presented in Figure 2. In general, the densities obtained for the foams lie within the range of 119.85 to 138.35 kg/m^3 or within 15% fluctuation.

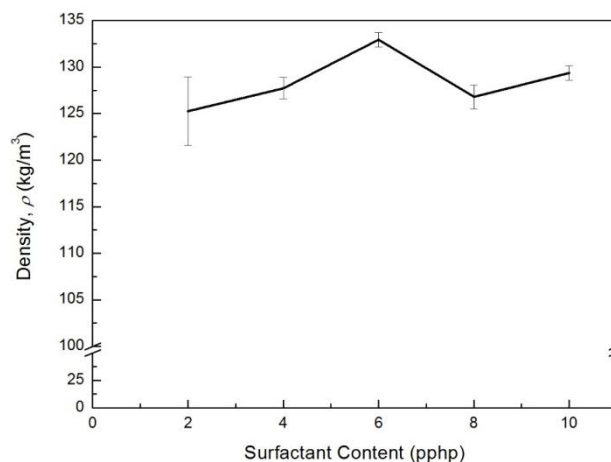


Figure 2 Densities of PU nanocomposites with various surfactant compositions

Referring to the graph, it can be observed that the foam densities fluctuates as the surfactant content is increased; which proves that blowing efficiency increase with increasing surfactant content [19]. However, excess surfactant content tends towards collapse as a result from the over stabilization of the cells in the foam [18] and compromising the stability of the foam, as proven by foam densities with surfactant contents higher than 6.0 pphp. From Figure 2, it can be seen the densities deteriorated beyond 6.0 pphp surfactant, while the sudden plummet of density for 8.0 pphp was believed due to the less inclusion of the polysiloxane into the PU foam, correlated with the results obtained for FTIR spectroscopy for the mentioned surfactant content.

3.4 Compressive Properties

The compressive strength of PU nanocomposite foams varying surfactant composition is illustrated in Figure 3.

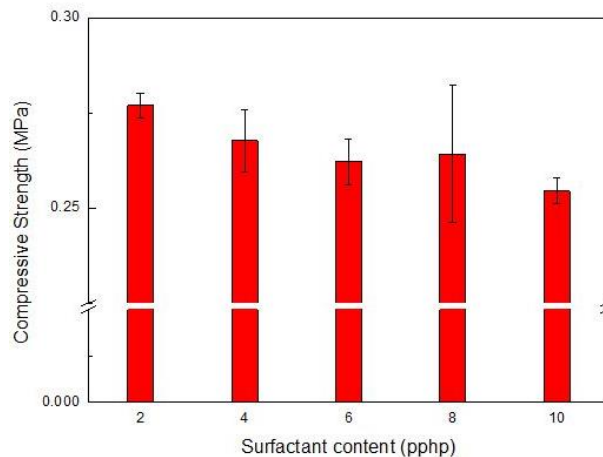


Figure 3 Compressive strength of PU nanocomposites foam with various surfactant compositions

With reference to the graph, it can be observed that at the increase of surfactant content, the compressive strength decreased gradually. This is because at higher content of silicone surfactant, it will act as plasticizer and over stabilized the cell foams [18], resulting in reduced mechanical properties. Upon adding the surfactant past its optimum value, the surfactant-polymer chains seem to aggregate together; resulting in increased internal bubble pressure due to lower surface tension [14]. Previous work have has also shown decrease in compressive strength for surfactant content over 2.0 pphp [19].

While it is made known that density governs the mechanical properties of closed-cell foams [1], this finding indicates otherwise. This is proven as density is highest at 6.0 pphp, while maximum compressive strength at 2.0 pphp. The foam's cell size is comparably smallest at 2.0 pphp, with no apparent change in the cell size detected past this optimum point. However, Lim *et al.* suggested that the compressive strength is rather dependent on the closed cell content [19]. Therefore, we believe that the reason of deterioration of compressive properties despite insignificant change in density is due to the inclusion of 4.0 wt.% of MMT nanoclay. As we mentioned earlier, nanoclay can also function as to control the foam's cell size; and the amount utilized in this study might have alter the surfactant cell-stabilizing effect. Study is currently underway to investigate the effect at lower nanoclay content.

4.0 CONCLUSION

In this preliminary study, we investigated the effect of silicon surfactant content on the structure and mechanical properties of palm oil-based PU foam reinforced with MMT nanoclay. The cell-stabilizing effect and mechanism of the silicon surfactant in the PU foam production has been demonstrated in this research. Deterioration in mechanical properties was also portrayed as excess amount of surfactant content. However, we believe the inclusion of MMT nanoclay into the PU matrix might have easily maximized the cell size-reduction effect of the silicon surfactant as the amount of nanoclay used might have induced clay agglomeration. A study is however underway to investigate this claim.

All in all, it can be concluded that the effect of surfactant content on the structure and mechanical properties of palm oil-

based PU foam reinforced with MMT nanoclay is not significant past its optimum point. For this research, the optimum point is obtained as 2.0 pphp, considering the maximum compressive strength achieved at this point.

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