Mechanical Properties of Palm Oil Polyol based Polyurethane Foam Reinforced Wollastonite Clay

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Abstract. The palm oil polyol based polyurethane (PU) foam reinforced wollastonite clay was prepared to study the effects of wollastonite clay addition towards the mechanical properties of PU foam. The palm oil polyol based PU foam with NCO: OH ratio of 1:1.22 was synthesized by mixing palm oil-based polyol, p-MDI, DMCHA, PMDETA, distilled water and incorporation of different amount of wollastonite clay powder (1, 3, 5 and 7 wt%). The FTIR analysis showed the absence of NCO peak at 2280 cm$^{-1}$ suggesting the complete conversion of isocyanates into urethane during the mixing process. Based on FESEM/EDX, it was found that the wollastonite clay were fitted into the PU matrix, whereby SEM showed an open cell structure of PU foam reinforced wollastonite clay. The density of PU foam reinforced wollastonite clay is increased as the amount of clay reinforcement is increased. This is due to the high viscosity of the mixture which hinder the foam from rising and hence produced a denser foam, thus reduced the pore sizes. Hence, the compressive strength increased as the density and wollastonite weight percentage in the foam is increased.

1. Introduction

Polyurethane (PU) foam is one of the most versatile class of specialty polymer. These foams are classified into three major classes; flexible, rigid and semi-rigid polyurethane foams. Rigid polyurethane foam possess a good adhesion, high durability and strength that make them an indispensable material in the construction industry and useful for insulating materials, polymeric concrete components, sealants and others [1].

Over few decades, research on polyurethane were usually performed using petroleum-based polyol. However, due to the environmental awareness as the arose of issue related to petroleum depletion and the escalation of the petroleum oil’s price, had raised concern among researchers to discover the alternative sources for production of polyurethane. Utilizing the natural based polyol mainly from vegetables oil in fabrication of PU foam have been done by researchers mainly using soy-bean oil, rapeseed oil and palm oil. The rigid PU foam derived from soybean polyols were found to have a better thermal and thermo-oxidative stabilities [2]. On the other hand, palm oil polyol has also been reported to exhibit good mechanical properties as it is employed in the fabrication of PU foam [3]. In addition, it is abundant and available in Malaysia. Hence, in this study, POP are used as replacement of petroleum based polyol which is believed improve the properties of the PU foam.
Developing a high class of polymeric materials has become a great interest among researchers in order to produce an improved properties and cost effective polyurethane foam. Besides choosing the types of reactants and processing technique, addition of fillers may potentially improve the properties of the foam. The properties of the polyurethane foam can be well-controlled and improved according to needs by adjusting the filler in terms of the types, shapes, sizes, volume and degree of dispersion [4]. In this present work, we investigate the possibility of using wollastonite clay as reinforcement materials in enhancing the mechanical properties of the rigid polyurethane foam palm oil polyol based for load bearing application. The relationship between pores size, density of the foam and the percentage of fillers addition are critically studied in order to identify the effect of filler addition in the PU foam.

2. Experimental

2.1. Material

Palm oil polyol (POP) and 2,4-aromatic methylene diphenyldiisocyanate (MDI) was obtained from Maskimi Polyol Sdn. Bhd, Kajang Selangor. The wollastonite clay was supplied by Ipoh Ceramic Sdn. Bhd. It was heated at 100˚C for 24 hours to remove the residue of water or volatile compounds entrapped in the clay. The calayst, pentamethyldipropylenetriamine (PMDETA) and dimethyl cetylhexamine (DMCHA) was purchased from Maskimi Polyol Sdn. Bhd.

2.2. Preparation of Palm Oil Polyol Based Polyurethane Reinforced Wollastonite Clay

The PU foam was prepared based on NCO:OH ratio of 1:1.22. Different weight percentage of wollastonite (1, 3, 5 and 7%) were added to reinforce the PU foam. Table 1 shows the composition of each reactant used in synthesizing PU foam. The palm oil polyol (POP), PMDETA and DMCHA were mixed together and distilled water was added as blowing agent. The mixture was mixed using standard propeller with speed 1300 rpm for 2 minutes followed by addition of wollastonite clay at different weight percentage and prolong mixing for one and a half minutes to enhance the homogeneity and obtain greater dispersion of clay in the polyols. MDI was then added into the mixture and stirred for 10 seconds then, the foam was left to rise and set in normal room temperature and atmospheric pressure for 16 hours before demoulded.

Table 1. The composition of reactants used in synthesizing Palm Oil Polyol Based Polyurethane Reinforced Wollastonite Clay.

| Sample | Wollastonite Clay Weight Percentage (%) | Wollastonite Clay (g) | p-MDI (g) | POP (g) | PMDETA (g) | DMCHA (g) | Distilled Water (g) |
|--------|----------------------------------------|-----------------------|-----------|---------|------------|-----------|---------------------|
| S1     | 0                                      | 0                     | 303.28    | 306.43  | 1.21       | 1.81      | 0.12                |
| S2     | 1                                      | 6.5                   | 289.58    | 350.29  | 1.40       | 2.10      | 0.14                |
| S3     | 3                                      | 19.5                  | 283.73    | 343.21  | 1.37       | 2.06      | 0.14                |
| S4     | 5                                      | 32.5                  | 277.88    | 336.13  | 1.34       | 2.02      | 0.13                |
| S5     | 7                                      | 45.5                  | 272.03    | 329.06  | 1.32       | 1.97      | 0.13                |

2.3. Characterization of Palm Oil Polyol Based Polyurethane Reinforced Wollastonite Clay

2.3.1. Fourier Transform Infrared Spectroscopy (FTIR). The chemical bond characteristic of the foam was determined using FTIR Spectroscopy (PerkinElmer Spectrum One FT-IR Spectrometer). A total of 4 scans were taken for each sample over the wavelength of 4000-600 cm⁻¹ at a resolution of 4 cm⁻¹.

2.3.2. Scanning Electron Microscope & Field Emission Scanning Electron Microscope/ Energy-disperse X-ray Spectroscopy (SEM/FESEM). SEM was used to determine the cellular structure
differences resulting from the use of different weight percentage of wollastonite clay. The sample of size 10mm x 10mm x 5mm were cut and coated with Au conductive layer were analysed using Hitachi TM3000 with accelerating voltages of 5keV. The wollastonite clay composition in polymeric matrix was captured using FESEM/EDX (SUPRA 35VP, ZEISS).

2.3.3. Free Rise Density (FRD). The paper cup (220 cm$^3$) are weighed before mixing. The foam was then stabilized for 10 minutes after stop rising. Weight of foam was recorded and the FRD was calculated as shown in equation 1.

$$Free\ Rise\ Density = \frac{[(weight\ of\ cup,\ g + foam,\ g) - (weight\ of\ cup,\ g)]}{volume\ of\ cup,\ cm^3} \times 1000 \quad (1)$$

2.3.4. Moulded Density (MD). Moulded Density was obtained based on method BS 4270: Part 1:1988 Method 2 by producing foam in the 24.5cm x 24.5cm x 6cm dimensional moulds. The moulded density was calculated based on equation 2.

$$Moulded\ Density = \frac{weight\ of\ foam,\ g}{volume\ of\ mould,\ cm^3} \times 1000 \quad (2)$$

2.3.5. Core Density (CD). Core Density was measured using method BS 4370: Part 1: 1988: Method 2. Rigid polyurethane foam was cut into 5 blocks with dimension 50mm x 50mm x 50mm. Each sample was weighted and dimension was recorded. The density of the blocks was calculated using equation 3.

$$Core\ Density = \frac{weight\ of\ block,\ g}{volume\ of\ block,\ cm^3} \times 1000 \quad (3)$$

2.3.6. Compressive Testing. The compressive test was carried out using Instron 5982 universal testing machine according to BS4370: Part 1 1988: Method 3. Samples with size of 50 x 50 x 50 mm$^3$ was compressed to 80% of its original thickness with crosshead speed 5 mm/ min at 23±2°C. The stress-strain curves obtained was used to determine the compressive strength.

3. Result and Discussion

3.1. FTIR analysis
FTIR analysis was done to study the completion reaction and identify the chemical bonding characteristic in PU foam. The foam spectrum of pristine PU foam and PU reinforced wollastonite clay at different percentage are illustrated in Figure 1.
The presence of hydrogen bonding can be monitored from the group of hydrogen bonded amine (H-NH) and remaining OH groups at 3316 cm\(^{-1}\). The C-H stretches was observed at 2926 cm\(^{-1}\) and 2854 cm\(^{-1}\) followed by peaks at 1511 cm\(^{-1}\), 1213 cm\(^{-1}\) and 1068 cm\(^{-1}\) which indicates the urethane linkages of N-H, C-N and C-O which confirmed the reaction between polyol and isocyanates had occured. Hydrogen bonded carbonyl group (H-CO) was observed at 1715 cm\(^{-1}\) which indicates the formation of inter-urethane hydrogen bonding between N-H and C-O. It can be seen that there is no trace of NCO peaks at 2280 cm\(^{-1}\) suggesting the complete reaction had occurred in formation of PU [5]. Extra peaks were expected to be found in the wavenumber range of 800-1250 cm\(^{-1}\) which is assigned to the asymmetric Si–O stretching modes within a SiO4 tetrahedron, the peaks in wavenumber range of 600-800 cm\(^{-1}\) are attributed by both Si–O–Si bond bending and symmetric Si–O stretching vibrations, and lastly those in the wavenumber range (400-600 cm\(^{-1}\)) are originated from O–Si–O bending and Ca–O stretching modes [6]. FESEM/EDX was used to observe the presence of wollastonite clay particle under the magnification level of 3000x at two different spot. From Figure 2, it was found that the wollastonite clay does fitted into the foam matrix as there is trace of calcium and silicon elements observed for 7% wollastonite reinforced PU foam.

![Figure 2. FESEM/EDX results of 7 wt% wollastonite reinforced polyurethane foam](image)

**3.2. Density and Pore Size Analysis of Wollastonite Clay reinforced PU foam**

The density of the wollastonite clay reinforced polyurethane foam was found to increase with the amount of wollastonite clay. Figure 3 showed the core and mould density calculated using the equation (2) and (3). The wollastonite clay have a relatively higher density value as compared to the polyurethane foam matrix, thus increase the overall density of the samples [7]. Besides, the viscosity of the mixture with wollastonite clay would also affect the density of the foam. The higher the amount of wollastonite clay added into the mixture, will increase the viscosity of the mixture. The high viscosity of the mixture will then retard the foam from rising which therefore produced a denser foam.

| Sample No. | Wollastonite Clay Weight Percentages, % | Pore Size, μm | Average | Standard Deviation |
|------------|----------------------------------------|--------------|---------|--------------------|
| S1         | 0                                      | 799.8        |         | 61.34              |
| S2         | 1                                      | 596.2        |         | 51.92              |
| S3         | 3                                      | 501.2        |         | 35.37              |
| S4         | 5                                      | 484.4        |         | 66.10              |
| S5         | 7                                      | 417.4        |         | 58.91              |

The pore size of the wollastonite clay reinforced PU foam is influenced by the amount of wollastonite clay in the mixture. The result shown in Table 2 shows that the pore size of the foam decreased as the amount of wollastonite clay is increased. The cell structure of the wollastonite reinforced polyurethane foam is an open-cell type as shown in Figure 4. In open-cell structure, the cell walls are broken and consist of mainly ribs and struts, thus provide better absorptive capability. It is revealed that S1 have fewer cells and larger cell size as compared to the composites foam having 1, 3, 5 and 7 wt% of
wollastonite clay. The average cell size value 800 µm of S1 was decreased to 596, 501, 484 and 417 µm with the incorporation of 1, 3, 5 and 7 wt% clay respectively. S3 showed a uniform cell size distribution as results from uniform distribution of nucleation agents in the foam matrix [8].

The decreasing of cell size due to the existence of wollastonite clay particles that exfoliate in the foaming system acting as a cell opener. During cell formation, the clay particles act as a nucleation site and since in cellular structure, there are more number of cells that start to nucleate at the same time while adequate gas are available for cell growth hence resulting into a more compact size of the cell [9]. Heterogeneous nucleation occurred faster than homogeneous nucleation as the nucleation barrier is much lower at the surface. Therefore, as the amount of wollastonite clay is increased in the formulation of foam, a smaller pore size and denser foam is obtained as compared to lower amount of wollastonite added in the polyurethane foam if the volume of both samples are the same [10].

![Graph of core density and mould density of the wollastonite reinforced polyurethane foam](image)

**Figure 3.** Graph of core density and mould density of the wollastonite reinforced polyurethane foam

![SEM images of wollastonite reinforced polyurethane foam’s cell structure at different wollastonite percentage in the foam](image)

**Figure 4.** SEM images of wollastonite reinforced polyurethane foam’s cell structure at different wollastonite percentage in the foam (a) 0%; (b) 1%; (c) 3%; (d) 5%; (e) 7% at 800X.

### 3.3. Compressive Strength of Wollastonite reinforced PU foam

Compressive strength is related to the load-bearing capacity that is an important factor in foam application. Thus, the effect of density towards mechanical properties was investigated. The relationship between density, compressive strength and the weight percentage of wollastonite are shown in Figure 5. It can be seen that the compressive strength of the foam linearly increased with the density and wt% of wollastonite in the foam. This is believed to occur due to well distribution of wollastonite clay within PU foam matrix and mixing process. The mixing of the particles in low viscosity monomer using high shear mixer resulting in higher rate of diffusion of composites into the matrix [8]. Thus, improved
interlayer interaction between the particles and the PU matrix resulting in denser foam formation with reducing cell size.

![Graph of compressive strength and density against the weight percentage of wollastonite clay](image)

Figure 5. Graph of compressive strength and density against the weight percentage of wollastonite clay

4. Conclusion

The addition of filler have improved the properties of PU foam. The correlation between filler percentage, density, pore size and compressive strength was successfully studied. The increment in filler percentage, density and compressive strength resulted in reducing the pore size, thus, improved the rigidity of palm oil polyol based polyurethane foam.

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