Effect of Filler Loading on Properties of Polyurethane/Clay Composites

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Abstract. This paper discusses about the effected of filler loading on properties of polyurethane/clay composites. Polyurethanes materials have been developed strongly in the world, proving it to be one of the most versatile polymers. Segmented polyurethanes are very versatile materials, which can display properties ranging from very soft thermoset elastomer to strong. The objective of this study is to investigate the behaviour of polyurethane/clay composites, in term of strength, swelling behaviour and morphology properties. Polyurethanes based on diisocyanate molecule with diol were prepared by stoichiometric reaction 1:1 and 1:2 ratios of diphenylmethane diisocyanate (MDI) and polyethylene glycol (PEG 400). In both ratios, 2%, 4%, 6%, 8%, 10% and 20% of clay were added as filler loading. Polyethylene glycol (PEG 400) and clay are mixed together to become homogenous around 300 r.p.m. at room temperature for 10 minutes. After that, the solutions mixture with diphenylmethane diisocyanate (MDI) and are mixed again for 15 minutes around 300 rpm. The effect of adding clay was assessed by several testing method; compression test, swelling behaviors, spectroscopy infrared (FTIR) study and scanning electron microscope. Compression test result shows, with increasing percent of clay, the strength are increase for both of the ratio, 1:1 and 1:2. For swelling behaviors, from swelling index, result 1:1 ratio is better than 1:2 ratio. From infrared spectroscopy observation, the clay structure improved the hard segment of polyurethanes/clay composites. SEM micrograph of surface polyurethanes/clay composites observation shows, the structure of cell is homogenous; it is proved that chemical solution and clay are mixed together.

1. Introduction
Polyurethanes are one of the most versatile polymer materials, and it have been developed strongly in the world, today. Polyurethanes foams have a largest market among polymeric foams, estimated at nearly two billion kilograms in the US alone [1, 2]. Polyurethanes have an excellent abrasion resistance and the properties of both rubber and plastics. Polyurethanes are used in various application including as a thermal insulation, cushioning, buoyancy, energy absorption (packaging), etc. Due to low-density behaviour, these materials have been used as an interior panel for aircraft, structural shapes, shipping manufacture, sport equipment and composite tooling. However, polyurethanes also have disadvantages, such as low thermal stability and low mechanical strength [2].
Polyurethanes are made by the reaction of diisocyanate and a diol (R(OH)2), therefore the inclusion of various chain extenders allows a huge range properties to be achieved [3]. Polyurethane foams are available on thermoset or thermoplastic materials, from flexible (soft) too rigid or from tough to stiff elastomers [4]. Mechanical properties are important considerations for structural or semi-structural application as reported by Xia et. al. Therefore, due to polyurethanes, foams are formed by polymerisation method and foam blowing occur simultaneously, the polymer structure must build up rapidly to support the fragile foam, and not too fast to stop bubble growth [1]. Usually, polyurethane foams is used as a core for the sandwich structures in conjunction with two face sheet materials around it [4]. Core increases the energy absorption capability of the sandwich structure, but due to the weak the internal failure of sandwich structure is propagates through the core in the event of impact loading. Thus, it is important to improve the properties of thermal and mechanical properties of the core structures, which is polyurethane foams. To overcome these disadvantages, the development of nanostructured polyurethane (PU)/montmorillonite (MMT) composites in recent years [5, 6]. Effect of clay type, clay content and PU molecular structure on clay dispersion in thermoplastic PU nanocomposites have been studied, whereby it have been found that clays exchanged with long chain oniumions and good compatibility with polyol [1,5,6]. However, as reported by Tien et. al. a good dispersion of clay in the polyurethane matrix have been achieved through the modification of MMT with containing more than two hydroxyl group [7,8,9].

The literature regarding the use of nanoclay improved the thermal insulation and aging properties of polyurethanes foam [1]. The earliest motivation for the use clay in this research, in order to study the potential of low cost alternative materials to produce high performance composites structures, with an existing materials, which is diisocyanate and diol. In this study, polyurethane/clay composites, as well as foams were prepared by polymerisation method with different clay configuration. The effects of strength, swelling behaviour and morphology structures were investigated.

2. Methodology

2.1. Materials
Diphenylmethane-4, 4'-diisocyanate were used as a diisocyanate material and were obtained from Merck Schuchardt, Germany. The diol compound were obtained from Fisher Scientific, United Kingdom, Polyethylene glycol 400. Materials for clay were obtained from Zhejiang Fenghong Clay Chemicals Company LTD, with 13µm (Smectite Clay).

2.2. Polymerisation Methods
The diisocyanate and diol involved were weighed into the reaction in a 1:1 and 1:2, as shown in Table 1, with different composition of clay. The process of polymerisation, was started with combination of polyethylene glycol 400 and were added with clay (wt%) depends on the weight composition. After that, the mixer is used to mix both material to be homogeneous structure on the rotation speed of 300 rotation per minute (rpm). Diphenylmethane-4, 4'-diisocyanate was added after a few minutes of mixing process, with a little water was poured in the composition. The water was used as a blowing agent, whereby it is a substance that is incorporated into a mixture for producing foam (polyurethane). The process repeated until the required configuration of polyurethanes are formed. The polyurethane sample were cured at room temperature before the sample was cut out according to standard.
Table 1. Synthesis of polyurethanes with different composition of clay

| MDI/PEG (v/v) | Clay (wt%) | Mixing (rpm) | Blowing agent (ml) |
|---------------|------------|--------------|-------------------|
|               | Mix 1     | Mix 2       | Mix 3            | Mix 4 | Mix 5 | Mix 6 | Mix 7 |
| 1:1 ratio     | 0         | 2           | 4                | 6     | 8     | 10    | 20    | 300  | 4    |
| 1:2 ratio     | 0         | 2           | 4                | 6     | 8     | 10    | 20    | 300  | 4    |

3. Results and Discussion

3.1. Mechanical Properties

Figure 1 shows the compression stress versus filler loading of polyurethane/clay composites for 1:1 ratio. It can be seen that, polyurethanes without clay have high compression stress compared with polyurethane/clay composites. The high compression stress, represent the hard segment is more influence on this configuration. The compression stress is decreased with increasing 2 wt%, 4 wt% and 6 wt% of clay. The compression stress at 2 wt% and 4 wt% is high compared with 6 wt% of clay in polyurethane/clay composites. However, if the 8 wt%, 10 wt% and 20 wt% of clay are added, the compressions stress is increased. It is proven that, with increasing more clay in configuration, the polyurethane/clay composites are return to become hard segment.

![Figure 1](image)

**Figure 1.** Compression stress versus filler loading of polyurethane/clay composites

Figure 2 shows the compression stress versus filler loading of polyurethane/clay composites for 1:2 ratio. The compression stress of polyurethane without clay are nil, due to soft segment are more influence on this ratio. However, with increasing clay as a filler loading, the compression stress increases. Based on the figure, it clearly shows with increasing of clay configuration for solution 1:2 ratio, from 2 wt%, 4 wt%, 6 wt%, 8 wt%, 10 wt% and 20 wt% of clay, the strength characteristic of polyurethane/clay composites are increases.
3.2 Swelling Behavior Analysis

Table 2 (a) and (b) shows the data of swelling index polyurethane which immersed in chloroform at 24 hour for 1: 1 and 1:2 ratio. For 1:1 ratio, shown the polyurethanes without clay and 20 wt% have a lower swelling index compared with others polyurethanes/clay composites solution. However, the result of swelling index for 1:1 ratio is not constant as expected. For 1:2 ratio swelling index, it shows gradually increases with increasing clay on solution. This proves that with increasing percent of clay, the cross linking in polyurethane/clay composites decreases for 1:2 ratio, whereas the cross linking in polyurethane/clay composites increases for 1:1.

Table 2. Data of swelling index of polyurethanes, which were immersed in chloroform at 24 hour for ratio; (a) 1:1 ratio, (b) 1:2 ratio

| Clay (wt %) | Swelling Index | Clay (wt %) | Swelling Index |
|-------------|----------------|-------------|----------------|
| 0           | 11.23          | 0           | 7.08           |
| 2           | 12.03          | 2           | 11.31          |
| 4           | 15.70          | 4           | 13.94          |
| 6           | 19.14          | 6           | 15.34          |
| 8           | 18.93          | 8           | 16.48          |
| 10          | 18.61          | 10          | 17.04          |
| 20          | 14.08          | 20          | 21.74          |

(a) (b)

3.3 Spectroscopic Infrared Analysis

Figure 3 (a) and (b) shows the spectra of polyurethanes with and without clay. As seen, the both figures, two peaks at 3339.5 cm⁻¹ and 1528.5 cm⁻¹ is N-H. The asymmetric stretching of the C=N bond is at 2366.3 cm⁻¹ The asymmetric C-H stretch range to widen to 2920-2950 cm⁻¹ and the C-O stretch is at 1228.3 cm⁻¹. However, in Figure 3(b) show the typical absorbing peak of Si-O bond exists at 1072.2 cm⁻¹. The absorption peak at 825.6 cm⁻¹ is Si-CH₃. The characteristic bond of the polyurethane/clay
composites at 1718.3 cm\(^{-1}\) as assigned to the carbonyl group (C=O). The peak appearing at 1734.5 cm\(^{-1}\) was attributed to the free carbonyl group (C=O). The correlation of both bonds (free carbonyl and carbonyl groups) is evidence of hydrogen bonding. The presence of hydrogen bonding in polyurethane improved the hard segment of polyurethane/clay composites.

![FTIR spectrum of polyurethane (MDI/PEG: 1:1); (a) Without clay, (b) With clay](image)

**Figure 3.** FTIR spectrum of polyurethane (MDI/PEG: 1:1); (a) Without clay, (b) With clay

3.4 Morphology surface structure of Polyurethane

Figure 4 shows the SEM micrograph of the surface of polyurethane without and with clay for 1:1 ratio, are considered for comparison. Figure 4 (a) shows the SEM micrograph without clay. It can be seen that the structures is uniform with a small cell with porosity [9]. Even though, it have a porosity, but the strength is high compared to other solution due to stoichiometric ratio with hard segment characteristic. Figure 4 (b) shows the surface of polyurethane/clay composites, whereby the cell is agglomeration with a small and large cell.
4. Conclusion

The increasing strength is obtained from compression test. It was showed that with the increasing percent of clay, the strength increased for both of the ratio. However, the compression test for 1:1 ratio shown, the result is not constant, due to the stoichiometric reaction is not suitable with added clay as a filler loading in order to improve their strength. However, if more clay added in the solution, the strength also increased. In swelling index for swelling behaviors, the result of 1:1 ratio is better than 1:2 ratio. High cross linking in polyurethanes structures was observed proportional with increasing more clay as a filler loading. However for 1:2 ratio, it have more soft segment, the swelling index value is high due to absorption of more chloroform from the solution. Therefore, cross linking in polyurethane/clay composites is lower for 1:2 ratio. The infrared spectroscopy showed an additional of clay improved the hard segment of polyurethane/clay composites and correlates with improved in hydrogen bonding performance. From SEM micrograph surface of polyurethane/clay composites, it was showed the structures of polyurethane/clay composites cell are homogenous. In general, it is observed that chemical solution and clay can be mixed and shaped as polyurethane/clay composites.

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