The Mechanical and Thermal Properties of Polyurethanes/Precipitated Calcium Carbonate Composites

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Abstract. The properties of polyurethane containing precipitated calcium carbonate (PCC) were studied. The PCC were produced from acetylene gas waste, and its usage as filler material for polymer were explored in this study. Present findings suggested the addition of 5 per hundred gram of PU(phr) significantly increases the shore A hardness to 39.2, in addition to improve the degradation temperature and specific gravity with decrease in water and oil absorptions capacity. The addition of 5 phr PCC to polyurethane improves the material structure and the morphology as calcium carbonate were dispersed when observed using microscopes. This research extends our knowledge of the addition of PCC to strengthen the mechanical and thermal properties of polyurethanes.

1. Introduction

Polyurethane (PU) presents in large range of mechanical properties [1] and commonly used as pigging in oil and gas industries with deep water flow line coatings and seals protection [2]. PU can be produced through polymerization reaction, where isocyanates react with polyols. The bond between the isocyanate group (-NCO) and hydroxyl group (OH) bond yield urethane (-NHCOO-) [3]. Urethane bond is the functional groups for polyurethane and it usually made either from polyester or polyether. Previous study conducted by Rutkowska. et. al. suggested polyether PU contains higher retention strength when compared to polyester PU [4].

Polyurethane has three dimension (3D) structure which is cross-linked and does not degrade easily by the application of heat. The reaction between two monomers such as formation of cross-linked networks or a huge number of linear prepolymers cross-linking routes can form thermoset polymers. The thermoset polymers have high properties compared to thermoplastic such as thermal stability, hardness and strength [5, 6].

Filler is added to a polymer so that a conjugated biphasic material can form [7]. The forces that applied to the matrix will be changed to another form and showed on the disperse filler phase [8]. Researchers have investigated few types of organic and inorganic fillers that can improve the properties of polyurethane. Among the
inorganic materials include: aluminium hydroxide, calcium carbonate, silica, dolomite, talc [9] and titanium dioxide; while most of the organic materials used are natural fibers and carbon black [10]. The increase in density and compression resistance is promoted by filler in PU flexible foam. However, the resilience is reduced and it contributes to a permanent deformation. Plus, fillers influenced the properties of PU such as water absorption, tear strength, oil absorption, the mechanical properties and morphology of PU [11]. Therefore, it is crucial to determine the amount of filler added so results of reliable quality can be obtained [12].

In order to reduce cluster that caused by interactions of particles and high surface energy, the surface modifiers of CaCO$_3$ with stearic acid is used. The adhesion properties wetting which involved two phases are affected [13]. In [14, 15] CaCO$_3$ nanofillers are been used to improve the PU tensile properties. CaCO$_3$ filler particles with micro-sized improve the properties of rheological, cost of composition and thermal stability of thermoplastic PU matrix [16] is reduced.

The adaptability of calcium carbonate as filler in flexible PU foam composite has been observed. Sabina et. al. [17] studied the properties of physico-chemical of flexible PU foam which containing the excess of commercial CaCO$_3$ and commercial CaCO$_3$ used in industry. The results show that the rise of hysteresis can cause deformations permanently and it can also harm the final product quality. Latinwo et. al. [18] investigated the distributions of particle size on the mechanical properties of flexible PU foam and the effect of CaCO$_3$ of different compositions. A study showed that filler which is finely divided has increased the hardness characteristics of the foam to compositions which is up to 35 wt%. Meanwhile, there is no significant improvement in the property of coarse filler. The elongation at break and tensile strength decreased when filler content is increased for all particle sizes.

Sepulcre-Guilabert et al. [19] showed that the thermal, mechanical, rheological, adhesion properties and surface of a TPU are not affected by the addition of natural micronized calcium carbonate filler. Without the net PU and filler interactions, the scarcity of filler influence was formed. It caused by the absence of surface functional groups in the filler and the large size of particles. Jiang et al. [20] investigated the effect fatty acid coating of PCC on the properties of mechanical and rheological of TPU. They demonstrated that a fatty acid coating a particular rheological behaviour produced decreased at high frequencies with PCC loading but storage modulus($G_\theta$) increased at low frequencies. The viscosity of the solvent-based TPU solutions is decreased with the addition of PCC. It is caused by the fatty acid coating partially removed from the particle surface of PCC which is being transferred to the TPU matrix.

2. Methodology

2.1 Materials
The prepolymer (MDQ 24163), chain extenders (BAYTEC D24), curative (1- butanediol) and additives (AAA) were obtained from Covestro Elastomers SAS, Romans cedex France. The catalyst that used was triethylenediamine (SD 2.4) and was obtained from Covestro AG, Leverkusen, Germany. The filler that added to the poyurethane is precipitated calcium carbonate (CaCO$_3$) and can be obtained from Mineral Research Centre, Ipoh, Malaysia.

2.2 Preparation of polyurethane
Prepolymer MDQ 24163 and calcium carbonate are stirred for three minutes. The calcium carbonate weight is varied from 0, 5, 10, 15 g, 20 and 25 phr . After they are mix, the mixture is heated to 40°C. All the ingredients are added except the curative (BDO) when the temperature reached 40°C. Stir the mixture for 15 minutes at 196 rpm in without heating. When 15 minutes have elapsed, the BDO is added to the mixture and stirred for 3 minutes. The mixture is poured immediately to the mold and then be heated in the oven at 70°C for 24 hours. After 24 hours, the sample is removed from the oven and cut into different size for different test purposes.
Table 1: The composition to produce polyurethane

| Raw materials                  | Percentage in mass (%) For every 100 g of PU |
|--------------------------------|---------------------------------------------|
| Prepolymer (MDQ 24163)         | 38.34                                       |
| Chain Extender (Baytec)        | 57.52                                       |
| Curative (BDO)                 | 4.14                                        |
| Additive (AAA)                 | 0.3                                         |
| Catalyst (SD 2,4)              | 0.4                                         |

2.3 Testing Method

**Fourier Transform Infrared Spectroscopy (FTIR)**

FTIR analysis was carried out in FTIR Thermo Fisher Nicolet C700 (Thermo Scientific, USA) to investigate the density of cross linking of the polyurethane. Each of the spectra was recorded as the average of 32 scans taken with a resolution of 4 cm⁻¹ and was collected at an operating wave number ranging from 4000 to 425 cm⁻¹. The FTIR analysis was performed to identify the N=C=O, O-H and H-N=C=O bonds.

**Optical Microscope**

The optical microscope uses lens and light system to magnify small samples’ images. The image of the optical microscope can be captured by normal light camera to generate a micrograph. Phenix brand optical microscope with Phenix Micro Image software were used.

**Scanning electron microscope (SEM)**

SEM analysis was performed to observe the morphology and dispersion of calcium carbonate in the polyurethanes. The scanning electron microscope that used is Leo 1450 VP SEM. Before examination, all the samples were covered with a layer of gold to get rid of the charge of electrons in the sample.

**Thermogravimetrical analysis (TGA)**

TGA is a technique that uses heat to observe the reaction and the physical changes of a material that provides a quantitative measure of any change in the mass of the polyurethane. A Netztech STA 449 F3 Jupiter model was used to study the range of temperature between 25 °C to 600 °C with a heating rate of 10 °C/min.

**Specific gravity (SG)**

The type MH 300A density meter with a static support for an immersion vessel above or below the pan was used to determine the SG of polyurethane. The sample in air was weighed and then immersed in distilled water with the help of sinker. The weight of the specimen was calculated.

\[
\text{Specific gravity of specimen} = \frac{a}{a+w} - b
\]

where \(a\) = sample in air weight, \(b\) = sample with sinker in water weight, \(w\) = totally immersed sinker weight

**Shore A Hardness**

The shore A hardness was performed in Eureka Efektif. Durometer type A was used when conducting the experiments. The samples were tested and readings were taken at four different points on the sample.
Water absorption
Water absorption test conducted in accordance with ASTM D570 and the sample size used in the experiment is 10 mm x 10 mm x 5 mm. The equation to calculate the mass of the sample after immersed in water and the results are recorded after 24 hours.

\[ M_w = \frac{W_t - W_o}{W_o} \times 100\% \]  

(2)

Where,

\[ M_t = \text{Percent increase in mass,} \%
\]
\[ W_t = \text{Mass of sample at time } t, \text{ g}
\]
\[ W_o = \text{original mass of sample, g}
\]

Oil absorption
Oil absorption test is conducted and the sample size used in the experiment is 25 mm x 25 mm x 3 mm. The equation to calculate the mass of the sample after 4 days.

\[ M_o = \frac{W_t - W_o}{W_o} \times 100\% \]  

(3)

where \[ M_t = \text{Percent increase in mass,} \%
\]
\[ W_t = \text{Mass of sample at time } t, \text{ g}
\]
\[ W_o = \text{original mass of sample, g}
\]

3. Results and Discussion

3.1 FTIR

FTIR measurements are performed to prove the bonds in the polyurethane. There is no drastic changes when calcium carbonate is added. Disappearance of peak at 2200-2300 cm\(^{-1}\) proved that there is no unreacted isocyanates left. For polyurethane without calcium carbonate, peaks at 3336.6 cm\(^{-1}\) corresponds to the NH stretching. Sharp peaks at 2956.1 and 1415.2 cm\(^{-1}\) indicate the presence of OH stretching variation. The CH\(_2\) bend are identified at the height of 1456.1, 1382.4 and 1311.4 cm\(^{-1}\). In addition, the peak at 1734.1 cm\(^{-1}\) is associated with the group C=O in polyurethane. NH bend is identified at the peak of 1598.1 and 1536.9 cm\(^{-1}\). The peak 1224.0 and 1174.2 cm\(^{-1}\) indicate C-O-C stretch while the peak 1080.1 cm\(^{-1}\) indicates C-N. In addition, the peak of 818.5 and 770.8 cm\(^{-1}\) are related to the CH bend.

Figure 1. FTIR spectra of pure polyurethane and polyurethane with 5g of type A and type B calcium carbonate
3.2 Morphological Analysis

The SEM images in Figures 2(a-b) showed the image of two different types of the calcium carbonate used at magnifications of 500 ×. Figure 3a illustrated the type A calcium carbonate existed in round and circular forms whereas Figure 2(b) type B calcium carbonate structure looked like needle structure. It was proved that calcium carbonate did not evenly distribute in the liquid PU mixture, and the existence of calcium carbonate agglomeration were observed. The optical microscope images of liquid PU were showed in Figure 3(a). The image showed granules of solid PU which indicated curing process took place and clear liquid phase indicated the unreacted mixtures. The mixture of viscous mixtures of PU and PCC morphology were shown in Figures 3(b-c).

The SEM images of cured neat PU and composite samples were shown in Figure 4. The cross section images indicated the presence of micropores in the neat and composite samples.

Figure 2. SEM of (a) type A calcium carbonate (b) type B calcium carbonate under magnification 500x.

Figure 3. Images of optical microscope of (top, left) PU without CaCO₃ (top, right) PU with 5g type A CaCO₃ (bottom) PU with 5g type B CaCO₃ under magnifications 10x.
3.3 Thermal Analysis

Based on the TGA curve, it showed the percentage of mass left for polyurethane without calcium carbonate and polyurethane with 5 g type A and type B calcium carbonate. The polyurethane showed the decomposition temperature between 190˚C and 600˚C and produced 9:51% residue for polyurethane without calcium carbonate. The decomposition temperature of
calcium carbonate was between 680˚C and 875˚C where carbon dioxide will be lost and calcium oxide was generated. Polyurethane with calcium carbonate had a higher residual mass. Higher values of this sample showed calcium carbonate containing inert compounds which are in correlation with EDS analysis.

The polyurethane showed one stage of decomposition and the maximum temperature for the decomposition was recorded. It was proved that the calcium carbonate was homogenously distributed throughout the polyurethanes samples as the percentage of mass left corresponds to the mass of calcium carbonate added.

![Figure 5](image1.png)
**Figure 5.** Thermal Gravimetric Analysis of polyurethane without calcium carbonate and polyurethane with 5g type A and 5g type B calcium carbonate

![Figure 6](image2.png)
**Figure 6.** Thermal Gravimetric Analysis of polyurethane without and polyurethane with calcium carbonate

### 3.4 Specific Gravity

There is an increment for the specific gravity when the mass of calcium carbonate increases. By comparing the density between the two graphs, it was found that the density of the PU with type A calcium carbonate higher than the PU with type B calcium carbonate. It has been verified that the size of type A calcium carbonate bigger compared to type B in SEM analysis. Specific gravity is proportional to the size of calcium carbonate. The higher the specific gravity was due to the formation of bigger number of closed size and the bigger facilitation of
calcium carbonate in the polyurethane. The bigger the mass of calcium carbonate, the particles move more efficiently which caused the relative density increases.

![Figure 7](image_url)

**Figure 7.** Specific gravity of polyurethane with increasing mass of calcium carbonate

### 3.5 Hardness

The effect of mass and size of filler on hardness of the polyurethanes were investigated. The polyurethane density played an important role which affects the mechanical properties. When the isocyanate index increases, the hardness increases. The matrix experienced plasticizing when the fillers are treated organically. When the temperature is high for long period of time, the hardness of the polyurethanes increases because over curing happened. At higher filler content, the impact strength and flexural modulus increases. Furthermore, incomplete curing and high closed cell caused the hardness decreases [22].

![Figure 8](image_url)

**Figure 8.** Hardness of polyurethane with increasing mass of calcium carbonate

### 3.6 Water absorption


Water absorption increases when the mass of calcium carbonate increases but decreases when achieve the optimum mass. The percentage of water volume were obtained after 24 hours. Less increment in water absorption volume is due to the number of closed cell. When the mass of calcium carbonate increases, the cell contents decreases which cause the water absorption decreases.

Saijun et al. conducted a study and showed that polymeric systems that high crosslink density will have lower water absorption [23]. When equilibrium stage achieved, the water absorption of polyurethane reached the saturation where all the 3-dimensional crosslinked network structure are filled with water molecules [24].

**Figure 9.** Water absorption of polyurethane with increasing mass of calcium carbonate

### 3.7 Oil absorption

Oil absorption increases when the mass of calcium carbonate increases but decreases when achieve the optimum mass. The percentage of oil absorption was measured for four consecutive day. Less increment in water absorption volume is due to the number of closed cell. When the mass of calcium carbonate increases, the cell contents decreases which cause the oil absorption decreases.

**Figure 10.** Oil absorption of polyurethane with type A calcium carbonate
4. Conclusion

The FTIR spectra did not show significant changes in the density of cross linking. Polyurethane with different size and mass of calcium carbonate have been produced. The morphology of calcium carbonate and polyurethane with and without calcium carbonate were obtained by using optical microscope and SEM. The result of TGA experiments showed that addition of filler increases the thermal stability of the polyurethanes. The results showed that specific gravity and hardness of the polyurethanes increases when the filler contents increases. The water and oil absorption showed increasing trend but decreased when achieved a saturated state.

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