Journal of Mechanical Engineering *Vol 19(1), 71-82, 2022*

Mechanical Properties of Green and Petroleum based Polyurethane as Grouting Materials

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ABSTRACT

In this study, polyurethane grouting materials (PUG) were prepared using two different types of polyol which were castor-based polyol (CPUG) and petrochemical-based polyol (PPUG). Four different ratios of polyol (OH) to isocyanate (NCO) were used in this study. The effect of different compositions of Isocyanate on mechanical properties were investigated and compared. The flexural strength, and compression strength shows the increment with the increase of the NCO composition. Optimum flexural strength, flexural modulus, and compression strength obtained at composition of PPUG4 and CPUG4 with the ratio of NCO: OH, 2.6: 1. PPUG gives a higher value of mechanical strength as compared to CPUG, however, results obtained for both types of polyurethane are in the range of industrial PU grouting properties grade. The decrease in cell wall of CPUG and PPUG with the increase of NCO:OH indicating the increment in cell wall interaction resulting higher mechanical properties of PUG

ISSN 1823-5514, eISSN 2550-164X

Received for review: 2021-05-10
Accepted for publication: 2021-08-23
Published: 2022-01-15

Keywords: *Polyurethane; Grouting Materials; Green Polyol; Mechanical Properties, Morphological Properties*

Introduction

Grouting is known as a technique that is widely used to repair and strengthen broken and loosened matrices [1, 2]. Polymer grouting technology is an excellent maintenance technology for infrastructure as it is economical and a very efficient technique to seal a crack in concrete infrastructures. Over time, a few problems arise such as settlement issues, crack, and formation of sinkholes on concrete infrastructures which resulted in a requirement of continuous maintenance that caused an increase in the budget spending. Therefore, low-cost maintenance using excellent grout material was introduced to solve settlement issues [3].

One of the materials that have been gaining attention is polyurethane as it exhibits extraordinary properties such as lightweight, good mechanical properties, low conductivity, and good thermal stability compared to the other materials and it also can adhere strongly to many substrates which make it useful in many applications [4, 5]. Besides, it can expand in a short time which makes it suitable to be used as grouting material to seal the crack on concrete infrastructures. Polyurethane grouts are closed-cell foam and rigid, from the exothermic chemical reaction between the main starting raw materials which are polyol and isocyanate

Currently, almost 90% of polyurethane production in the industries uses petroleum-based polyol as their main component [6]. At present, there are a few concerns that arise due to the consumption of petrochemical-based polyol in production of polyurethane which is the raw material such as crude oil and coal that have a rapid rise in their prices and require a high technology processing system [7, 8]. Therefore, green polyol was introduced to replace petrochemical-based polyol and to overcome the problem that arises.

Castor oil is one of the natural oils that can be used directly as a polyol without any chemical modification due to the presence of the OH functional group in its chemical structure [9]. The NCO/OH ratio of PUG was varied to produce rigid PUG with excellent physical and mechanical properties. Isocyanate to Hydroxyl (NCO/OH) ratio is defined as the ratio between two-parts where the first part contains NCO while the other part contains OH functional group [10]. This study aims to produce rigid castor-based PUG that meets the industrial standard of grouting materials and to compare the properties between petrochemical-based PUG and castor-based PUG.

Methodology

Materials

The chemicals used in this research were castor oil (OH value: 161.62 mg/KOH, equivalent weight: 347 $gmol^{-1}$) supplied by Progressive Scientific Sdn. Bhd (Taman Batu, Jalan Batu Caves, Selangor), synthetic polyol, poly propyleneoxy sucrose (OH value: 414 mg/KOH, equivalent weight: 135.51 $gmol^{-1}$), 4,4-methylenediphenyl diisocyanate (NCO content: 31%, molecular weight: 360) where both type of polyol were supplied by Growchem Sdn. Bhd., surfactant (polyalkyleneoxide methylsiloxane copolymer) manufactured by Momentive Amer Ind. which act as stabilizer, blowing agent (1,1-dichloro-1-fluoroethane) supplied by Airgas USA to trigger the foaming of PUG, blowing catalysts (dimethylcetylhexamine) that act as blowing enhancer and gelling catalyst (pentamethyldipropylenatriamine) which trigger the gelling of PUG.

Preparation of CPUG and PPUG foams

Table 1 shows the formulation of CPUG and PPUG foams. The first step in the fabrication of CPUG and PPUG involve the mixing of polyol with a blowing agent, surfactant, and catalyst by using a mechanical stirrer at 3000 rpm for 2 minutes [11]. Then, isocyanate was added into the mixture and stirred at 3000 rpm for 20 seconds [9]. After that, the mixture was poured in an acrylic mould and conditioned at room temperature for about 24 hours for curing and hardening [12]. The sample was demoulded and left conditioned at room temperature for about 36 hours before going for testing and analysis. The same step was used to produce CPUG and PPUG with different NCO:OH composition.

Table 1. Formulation of CPUG and PPUG foams

Samples		NCO/OH ratios
Petrochemical -based PUG (PPUG)	PPUG1	2:1
	PPUG2	2.2:1
	PPUG3	2.4:1
	PPUG4	2.6:1
Castor-based PUG CPUG	CPUG1	2:1
	CPUG2	2.2:1
	CPUG3	2.4:1
	CPUG4	2.6:1

Characterizations of CPUG and PPUG foams

Density of polyurethane sample was calculated in two stages which were before and after the production of polyurethane grout. The testing was conducted according to ASTM D7487-08 (Polyurethane foam cup test) to investigate the free rise density of samples and BS4370: Part 1: 1988 Method 2 (Method of test for rigid cellular materials: Determination of apparent density) to study the core density of samples. The test was repeated four times for each composition. The free rise density of polyurethane grout was calculated as Equation 1 while core density was calculated as Equation 2.

$$FRD, kg/m^3 = \frac{[Weight\ of\ cup\ (g) + \ weight\ of\ PU(g)] - [weight\ of\ cup\ (g)]\ \times\ 1000}{Volume\ of\ cup\ (cm^3)} \quad (1)$$

$$CD, kg/m^3 = \frac{Weight\ of\ PU\ block\ (g)\ \times\ 1000}{Volume\ of\ PU\ block\ (cm^3)} \quad (2)$$

Flexural tests were examined based on the ASTM D 790, ISO178 method at 3-point bending. Four samples from each composition with a dimension of 190 x 13 x 10 mm were tested using Instron Flexural Testing Machine with a support span of 75 mm and bending speed of 4.1 mm/min. The compression strength was determined according to ASTM D 395 method B using Shimadzu Universal Compression Testing machine with crosshead speed movement of 50 mm/min and sample dimension of 50 x 50 x 50 mm. The test was repeated on four different samples for each composition. Scanning electron microscopy (SEM) was conducted on both CPUG and PPUG samples according to ASTM E 2089 method using SUPRA field scanning electron microscope with a voltage of 5 Kv and 4.5 mm to 7.5 mm of WD at 100X magnification. The sample surface was coated with 10 nm of gold layer before the analysis.

Results and Discussions

Density

Table 2 shows that free rise density and core density of both CPUG and PPUG increased with increasing NCO:OH ratio. The increase of isocyanate led to the increment of foaming reaction resulting in higher cellular foams and more compact arrangement of cellular foams produced in both types of PUG matrix [13]. Overall, the free rise density of CPUG and PPUG are in the range of 202.15 kg/m^3 to 222.1 kg/m^3 and 150.58 kg/m^3 to 195.30 kg/m^3 respectively.

Table 2: Density of PPUG and CPUG

	Free Rise Density (kg/m^3)		Core Density (kg/m^3)	
Type	CPUG	PPUG	CPUG	PPUG
2.0:1	202.15	150.58	188.27	139.8
2.2:1	209.88	171.67	195.21	142.7
2.4:1	219.17	180.83	268.56	155.39
2.6:1	222.1	195.3	268.86	173.96

The core density of CPUG and PPUG are in the range of 188.27 kg/m^3 to 268.86 kg/m^3 and 139.80 kg/m^3 to 173.96 kg/m^3 respectively. In comparison, the overall free rise density and core density of CPUG are higher compared to PPUG. This is because castor polyol has secondary OH that make its reactivity and blowing efficiency of the mixture less than petrochemical-based polyol which have primary and secondary OH [14]. These resulted in low reaction time and lead to formation of large cellular foam size of CPUG as compared to PPUG. The presence of hydroxyl group in the middle chain of castor polyol also led to high steric hindrance which restricted the crosslinking between polyol and isocyanate [14]. These resulted in lower crosslinking density of CPUG compared to PPUG. Despite that, the results obtained for both CPUG and PPUG were in parallel with commercial PUG's density where the density of polyurethane grout was in the range between 90 kg/m^3 to 360 kg/m^3 [13]. Typically, high density polyurethane is considered as a lightweight material [15]. Therefore, it is considered as the best material in grouting applications as there will be very little additional weight being transferred to the part of repairs. This helps to minimize the chances of resettlement [15].

Flexural properties

In Figure 1, flexural strength for both CPUG and PPUG increase with the increase of NCO:OH composition. The optimum flexural strength was achieved by PPUG4 and CPUG4 with a value of 15.53 MPa and 11.01 MPa respectively. The result obtained for both PPUG and CPUG samples were similar to the previous result which stated that flexural strength of PU grout increased with the increase of density while the rising of PU grout density was directly related to the increased of NCO:OH ratio [9,13,16]. The density and flexural strength of both type of PU is increasing with the increasing of NCO:OH. A previous study reported that the flexural strength increases with the increased density of the foam [17]. This is because the increase of density was attributed to the increase of urethane crosslinking and cellular foams formation in the PUG matrix [16]. The high number of cellular foams led to the increment of interfacial bonding between the cellular foams in the PUG matrix hence, causing the increase of flexural strength.

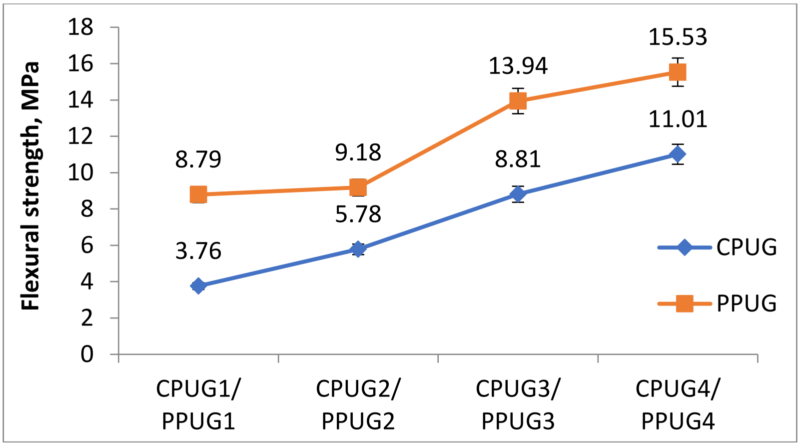

Figure 1: Flexural strength of CPUG and PPUG samples.

Based on Figure 2, the flexural modulus of both type of samples rapidly increased with the increment of the NCO:OH composition. PPUG4 had the highest flexural modulus with a value of 1299.25 MPa while CPUG4 had the highest flexural modulus with a value of 1069.5 MPa. The increase was attributed to the increase in urethane crosslinking which resulted in an increase of chain stiffness in both types of PUG matrix. These provided both CPUG and PPUG an excellent interfacial interaction between cellular foams in their matrix which enabled them to resist deformation when the stress was applied [18]. Overall, PPUG samples had a higher flexural strength and flexural modulus compared to CPUG samples. Despite that, the flexural strength and modulus of both PPUG and CPUG were in parallel with previous research that reported flexural strength of PU grout produced in their research was in the range of 2.8 MPa to 13.4 MPa while their flexural modulus was in the range of 21 MPa to 985 MPa [19].

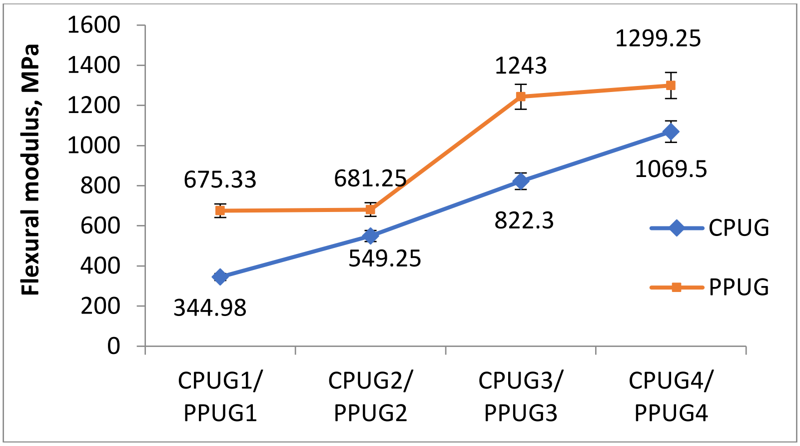

Figure 2: Flexural modulus of CPUG and PPUG samples.

Compression strength

Based on Figure 3, the compression strength of samples increases with the increasing NCO:OH composition. The increase of NCO:OH composition increased the hard part of PU which was NCO functional group. Therefore, more crosslinking formed between OH and NCO functional groups and thus increased the urethane linkage in CPUG and PPUG matrix samples [10]. The density of CPUG and PPUG steadily increased with the increase of the NCO: OH ratio. This was due to the increment of cellular foams and the more compact arrangement of foams in both types of PUG matrix [9]. This finding was in agreement with previous work done which stated that the compressive strength of PU foam increased with the increase of NCO:OH ratio [20]. As a comparison, the compression strength of PPUG samples was higher than CPUG. PPUG samples were produced from petroleum-based polyol that had a higher OH value which resulted in a higher crosslinking reaction and formation of an interchain network [21]. Nevertheless, the compression strength of CPUG and PPUG were in agreement to the previous result which reported that the compression strength of PUG having densities around 100-300 kg/m^3 in their research was in range between 1-5 MPa [22].

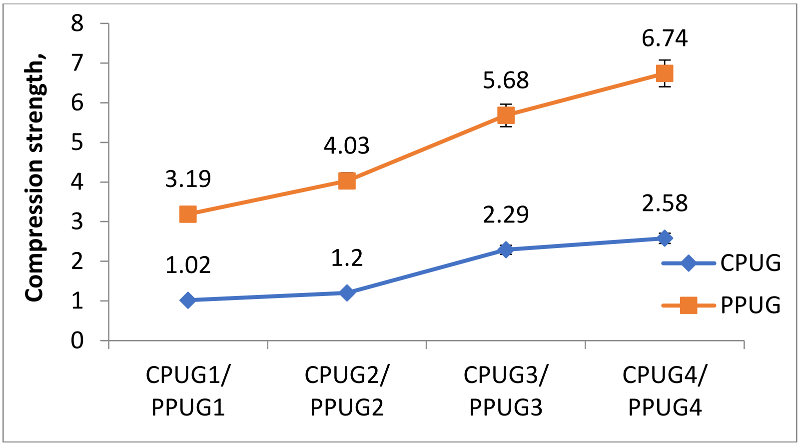

Figure 3: The compression strength of CPUG and PPUG samples.

Surface morphological analysis

Both PPUG and CPUG samples had a closed cell of foams with the spherical and polyhedral shape of foams. Exothermic reaction between polyol and isocyanate triggered the evaporation of the blowing agent into the gaseous phase which caused the formation of small bubbles in the PUG matrix [21]. Based on Figure 4, the diameter of the cell foam decreased with the increase in NCO:OH ratio. The isocyanate used in the formulation also increased which increased the allophanate crosslinking. These lead to the increase of cell wall's elasticity which makes the growth of the bubbles become harder that resulted in a decrease in the size of cell foam [21]. The overall range of cell foam's diameter for PPUG samples was between 215.1-359.2 µm. The decrease of PPUG cell walls with the increasing of NCO:OH composition indicates that their surface area increases which leads to higher cell wall interaction. These lead to an increase in mechanical properties of PPUG.

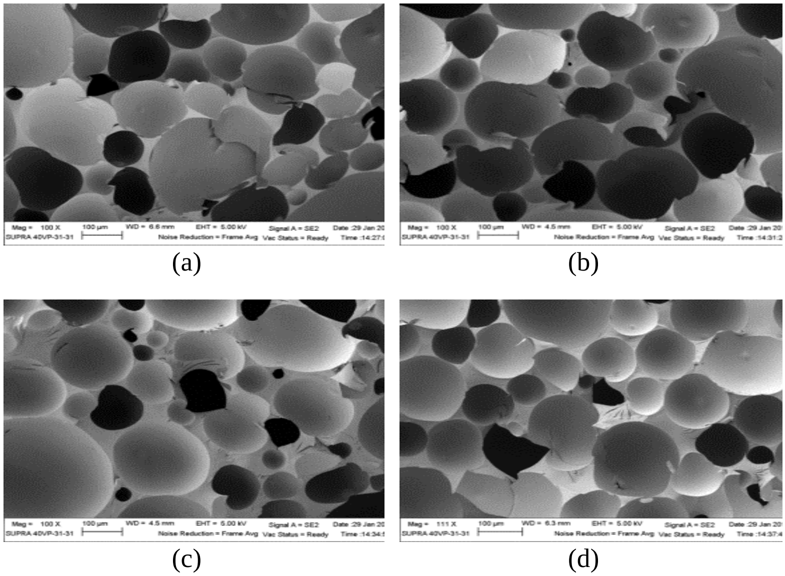

Figure 4: SEM images of PPUG samples (a) PPUG1, (b) PPUG2, (c) PPUG3, and (d) PPUG4.

Based on Figure 5, the cell foam's diameter of CPUG samples also decreased with the increase of the NCO:OH ratio. The overall range of the cell foam's diameter for CPUG samples was between 286.8-478 µm. Apart from that, the foam cell diameter of both PPUG and CPUG samples was inversely proportional with their density. It was because the smaller the diameter size of cell foam in the PUG matrix, the higher the thickness of the cell walls which increased the weight of PUG and resulted in a higher density of samples [22, 23]. The increase of compression strength for CPUG samples also can be explained by the decreasing of cell foam diameter. This was in complete agreement with previous findings which stated that the compressive strength of plastic foams under high compressive loads increased when the cell size of the foam decreased [24]. As a comparison, PPUG samples had a lower cell foam diameter compared to CPUG samples, indicate higher surface area and good bonding ability.

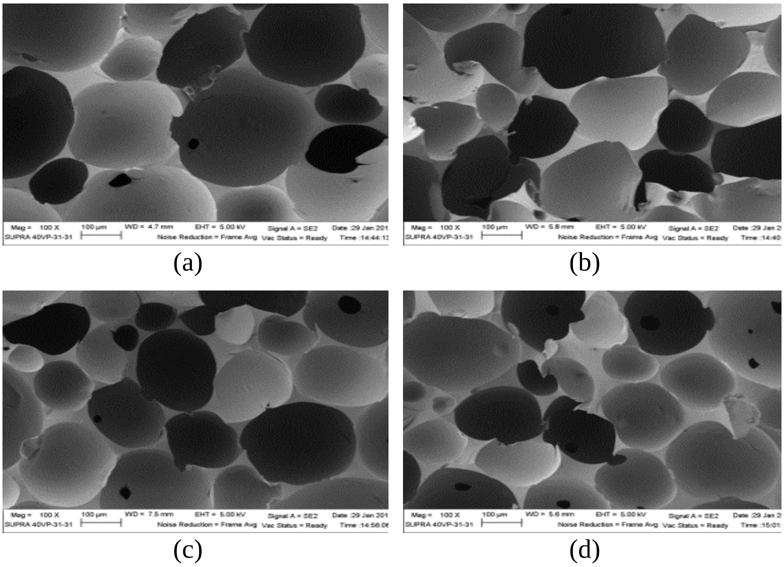

Figure 5: SEM images of CPUG samples (a) CPUG1, (b) CPUG2, (c) CPUG3, and (d) CPUG4.

Conclusion

In summary, the flexural strength, and modulus for both types of samples increased with the increment of the NCO:OH ratio. PPUG4 and CPUG4 with an NCO:OH ratio of 2.6:1 gave the optimum result for all mechanical properties. The closed, packed arrangement of the cell foam can be observed by SEM explaining the high value of flexural strength, flexural modulus, and compression strength achieved by PPUG4 and CPUG4. PPUG shows higher mechanical properties compared to CPUG. However, all the results obtained are still in the range of grouting materials properties. CPUG could be an alternative and environmentally friendly material for grouting applications.

Acknowledgement

The authors acknowledge research grant 600-RMC/GPK 5/3 (154/2020) and Universiti Teknologi MARA for the research facilities.

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