

Effect of NCO/OH Ratio on Physical and Mechanical Properties of Castor-Based Polyurethane Grouting Materials

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Abstract. This research focused on fabrication of castor-based PU grout (CPUG) using castor oil with OH value of 161 mg/KOH/g and MDI with NCO content of 31%. CPUG were prepared based on different NCO/OH ratio. The effect of NCO/OH ratio on the foam reaction time, density, rheology, morphological and mechanical properties were investigated. The result obtained shows that the rise time of CPUG decreased with the increased of NCO/OH ratio while tack free time increased with the increased of NCO/OH ratio. Morphological properties shows that CPUG consist of closed cell of foams and the diameter of a single cell foam decreased with the increased of NCO/OH ratio. The apparent density, rheology index, flexural strength, flexural modulus and compression strength of CPUG significantly increased with the increased of NCO/OH ratio. CPUG's apparent density was in the range of 230.23 kg/m³ while rheology index of CPUG was between 1.74 to 2.43 cm/g. Both values obtained were in the range of industrial PU grout's density and rheology index (214 kg/m³ & 1.48 cm/g). CPUG with NCO/OH ratio of 2.6:1 give the best flexural and compression strength with a value of 11.01Mpa and 2Mpa respectively. Flexural and compression strength of CPUG were tantamount to the industrial PU grout's properties which the average of flexural strength was about 7.4MPa while the average of compression strength was about 2MPa.

1. Introduction

The existence of crack on concrete bridge deck have been raise the concern of the bridges users as the crack can spread until a hole forming on concrete bridge deck which can cause traffic problem and also decrease the bridge's service life. Polyurethane grouting is a mature technology used to seal the cracks that occur on concrete bridge deck. Nowadays, polyurethane grouting material has been gaining a lot of attention from manufacturers from all over the world due to its extraordinary properties such as light weight, good permeability and good mechanical performance [1]. Polyurethane grouts is a rigid, closed cell foam which produced from reaction of two main components which are isocyanate as hard segment and polyols as soft segment [2]. Most of available polyurethane grout in the industry are petrochemical-based polyurethane. However, petrochemical-based polyurethane is expensive due to the increase in price of petrochemicals and crude oils. The high demand of petrochemicals and crude oil in the industries and also the high cost of production of petrochemical-based polyurethane grouts due to complex extraction process of petroleum contribute to the high price of petrochemical-based polyurethane [3]. The production of petrochemical-based polyurethane increase the environmental

concern as the extraction process of petrochemical-based polyol caused environment pollution due to the released of waste product formed during extraction process to the surrounding. Therefore, green grout polyurethane was developed to replace petrochemical-based polyurethane grout. Green grout polyurethane can be produced from natural polyol such as vegetables-based polyol. A few types of vegetables oil that is highly unsaturated and can be used as polyol are soybean oil, corn oil, linseed oil, sunflower oil, safflower oil, tung oil, olive oil and castor oil [4]. However, most of the vegetable oils must be synthesized in order to get the polyol except for castor oil which is a very unique vegetable oil that has hydroxyl group in its chemical structure which enable it to be use directly as a sole polyol without any modification process. Castor oil has low hydroxyl number which led to a low reactivity and with the use of castor oil as a sole polyol in production of PU, semi-flexible to semi-rigid PU foams is formed [4]. It is hard to formulate rigid PU grout by using castor oil. Despite that, rigid CPUG with excellent mechanical properties still can be fabricated which is by varying the NCO/OH ratio of CPUG. NCO/OH ratio is defined as equivalent ratio between the materials containing NCO and OH groups [5]. The increase of NCO/OH ratio led to an increase of isocyanate which can enhance the formation of covalent crosslinking in CPUG samples resulting CPUG samples with excellent mechanical properties [6]. In this study, the effects of NCO/OH ratio on foam reaction time, density, rheology, morphological and mechanical properties of CPUG were investigated.

2. Experimental

2.1. Materials

The chemicals used in this research were castor oil (hydroxyl value : 161.62 mg/KOH/g, equivalent weight : 347gmol^{-1}) distributed by Progressive Scientific Sdn. Bhd, isocyanate (4,4-methylenediphenyl diisocyanate) with NCO content : 31% , molecular weight : 360, supplied by Growchem Sdn. Bhd., surfactant (polyalkyleneoxidemethylsiloxane copolymer) manufactured by Momentive Amer Ind., blowing agent (1,1-dichloro-1-fluoroethane) supplied by Airgas USA, pentamethyldipropylenetriamine (PMDETA) act as blowing catalyst and dimethylcetylhexamine (DMCHA) act as gelling catalyst which both catalyst were supplied by Huntsman (Singapore) Pte Ltd.

2.2. Castor-based Polyurethane Grout Preparation

Four different compositions with varied ratios of castor oil and isocyanate were fabricated. The compositions used were explained in Table 1. Castor oil (100pbw), blowing agent (1pbw), surfactant (2pbw), gelling catalyst (0.4pbw) and blowing catalyst (0.4pbw) were mixed in a plastic using mechanical stirrer for about 2 minutes at 3000 rpm. Then, the hard part, isocyanate(NCO) was added into the mixtures and mixed at 3000 rpm for about 20 seconds. After that, the samples was poured into an acrylic mould and conditioned at room temperature for about 24 hours. Later, the samples were demoulded and conditioned at room temperature for about 36 hours before being tested [7].

Table 1. CPUG formulations.

	NCO/OH ratio
CPUG 1	2 : 1
CPUG 2	2.2 : 1
CPUG 3	2.4 : 1
CPUG 4	2.6 : 1

2.3. Characterizations and Testing

Foam reaction time such as cream time, rise time and tack free time were determined during the fabrication of CPUG according to method ASTM D7487-13. The density of each CPUG samples were determined according to method BS: Part 1 : 1988 Method 2 which involved the measurement of four CPUG block samples from each composition with a dimension of 50 X 50 x 50mm. The rheology

properties of CPUG was determined by pouring CPUG into a clear hose having a diameter of 10mm. CPUG sample was poured in a direction which was opposite to the earth gravity and it was let to flow down the hose until it stop flowing and expanding [7]. Then, the rheology index of CPUG was calculated according to the recorded flow distance and total weight of CPUG used. Scanning electron microscopy (SEM) was conducted on CPUG samples according to ASTM E 2089 method with 100X magnification. CPUG's surface was coated with about 10-20 nm of gold before the analysis started and the cell morphology of CPUG was examined. Flexural properties was examined based on ASTM D 790 method with a compression speed of 4.1mm/min and the sample dimension of 3.2 X 12.7 x 125mm. Compression properties of CPUG was determined according to ASTM D 395 method B with crosshead speed movement of 50mm/min and sample dimension of 50 X 50 X 50mm.

3. Results and Discussion

The foam reaction time, rheology index, apparent density and mechanical properties of CPUG were presented in Table 2.

Table 2. The foam reaction time, rheology index, apparent density and mechanical properties of CPUG

Samples	Foam reaction time (s)			Rheology index (cm/g)	Apparent density (kg/m ³)	Flexural strength (MPa)	Flexural Modulus (MPa)	Compressi on strength (MPa)
	Cream time	Rise time	Tack free time					
CPUG 1	3	340	430	1.74	188.27	3.76	344.98	1.68
CPUG 2	4	320	435	1.89	195.21	5.78	549.25	1.86
CPUG 3	4	300	470	2.25	268.56	8.81	822.30	2.00
CPUG 4	4	280	475	2.43	268.86	11.01	1069.50	2.00

3.1. Foam reaction time

Cream time is the time taken by CPUG to start foaming after the stirring of raw materials. Figure.1 shows that the cream time increased with the increased of NCO/OH ratio up to 2.2:1 which the cream time increased from 3s to 4s. Then, it remain constant at 4s for CPUG with NCO/OH ratio of 2.2:1 up to 2.6:1. The overall range of cream time for CPUG was 3-4s. The values obtained correlate satisfactorily with previous finding which stated that rigid polyurethane foam can start foaming between 2s to 7s [8]. NCO/OH ratio did not much influence the cream time of CPUG as there was not much difference in the cream time of CPUG samples.

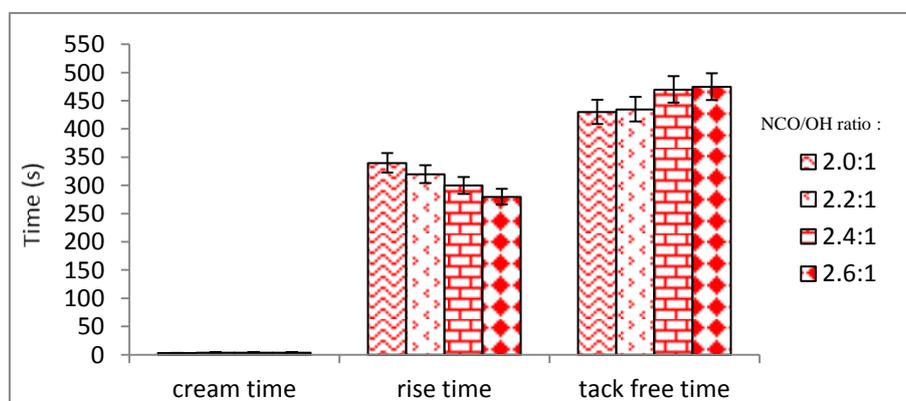


Figure 1. CPUG reaction time.

The rise time is the time taken by freely rising foam of CPUG to expand. The rise time of CPUG decreased with the increased of NCO/OH ratio as higher NCO/OH ratio appeared to enhance the foaming reaction of CPUG [9]. As the NCO/OH ratio increased, the exothermic reaction that took place in the system increased which triggered the foaming process as more gaseous from blowing agent vapourize and trapped in closed cell of the foam which at the end resulted a faster foaming reaction [10]. The overall range of rise time for CPUG was between 280-340s. The values obtained was slightly differ from previous findings. This may caused by the use of castor oil as a sole polyol which exhibit low OH value that affect the reaction rate of PU. On the other hand, the tack free time of CPUG increased with the increased NCO/OH ratio. Tack free time is the time taken by CPUG to start loses its stickiness on the outer skin of the foam which indicate the surface cure time of CPUG. The overall range of tack free time for CPUG was 430-465s. The increased of NCO/OH ratio resulting in increased of unreacted monomers (NCO) in CPUG sample which caused a stoichiometric imbalance between the reacting groups. The unreacted NCO had a low free energy which make them to be exposed on free surfaces and resulted a stickiness of CPUG samples that led to an increase of tack free time [11].

3.2. Apparent density

Apparent density is the overall density which include the skin of CPUG. In figure 2, it is observed that the apparent density of CPUG samples increased with the increased of NCO/OH ratio. This is parallel to the previous research which stated that the increased of NCO/OH ratio resulted an increase of density of PU foam [9]. The highest apparent density was achieved by CPUG produced using NCO/OH ratio of 2.6:1 with a value of 268.86 kg/m³. High density of CPUG was directly related to crosslinking and the foam rigidity as the increased of NCO/OH ratio led to the increased of hard segment in CPUG samples [9]. The increased of hard segment (NCO) caused the formation of intensive urethane and allophanate crosslinking in CPUG samples which led to increase of CPUG's density. The allophanate crosslinking is defined as a side reaction that occurred when the free isocyanate or unreacted NCO groups in CPUG samples react with the urethane formed [11]. The overall range of CPUG' apparent density obtained was between 188.27-268.86 kg/m³. The value obtained was consistent with previous research which stated that the density for PU grout was in range between 80 to 500 kg/m³ [12].

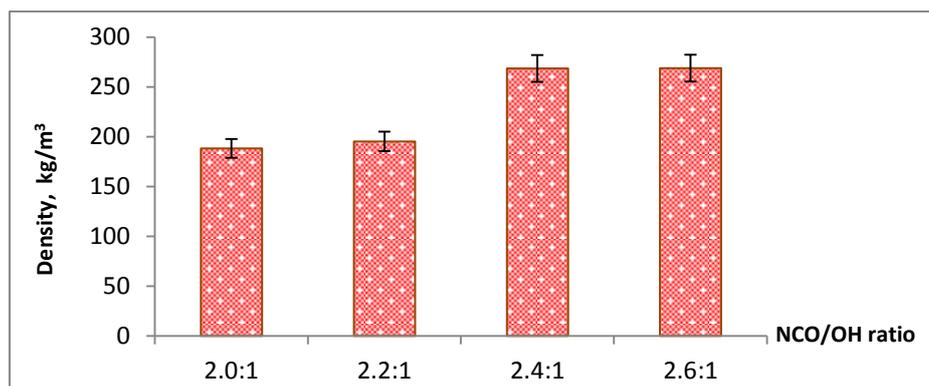


Figure 2. Density of CPUG samples.

3.3. Rheology properties

Rheology properties is one of the important properties that need to be measured in relation with the final application of CPUG. The rheology test was conducted in order to identify the ability of CPUG to expand and flow which simulate the rheology of CPUG when being injected into the crack on concrete bridge deck. Figure 3 shows that the rheology index increased steadily with the increased of NCO/OH ratio. It was due to the increased of foaming reaction of CPUG which resulted an increase of rheology index of the samples. CPUG produced using NCO/OH ratio of 2.6:1 had the highest ability to flow and expand as it exhibit the highest rheology index which was 2.43cm/g compared to the other

CPUG samples. The rheology index obtained in this research concurs well with the value obtained in previous findings which stated that the best range of rheology index for PU grouting material was between 0.4cm/g to 5cm/g [13]. As NCO/OH ratio increases, the rate of foaming reaction will increase thus resulted an increase of the expandability of the foam which led to increase of rheology index [9].

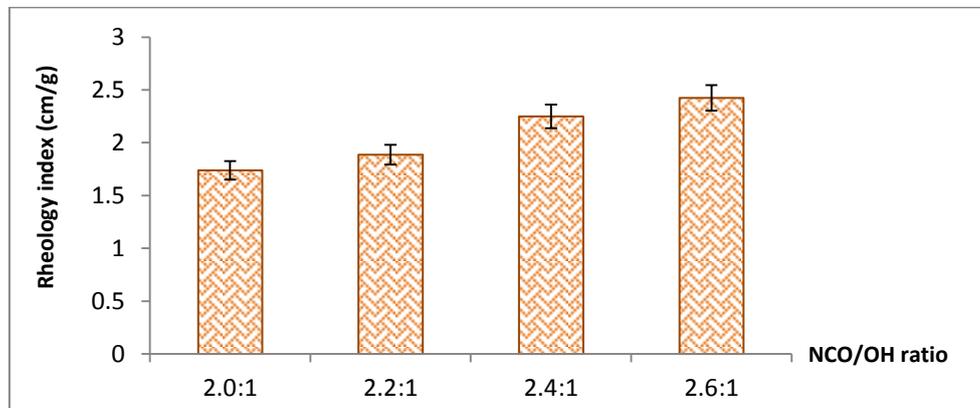


Figure 3. Rheology index of CPUG samples.

3.4. Flexural Properties

Figure 4 and Table 2 show that the flexural strength of CPUG samples increased with the increased of NCO/OH ratio. CPUG with NCO/OH ratio of 2:1, 2.2:1 and 2.4:1 had flexural strength of 3.76Mpa, 5.78Mpa and 8.81Mpa respectively. CPUG with NCO/OH ratio of 2.6:1 had the highest flexural strength which was about 11.01Mpa.

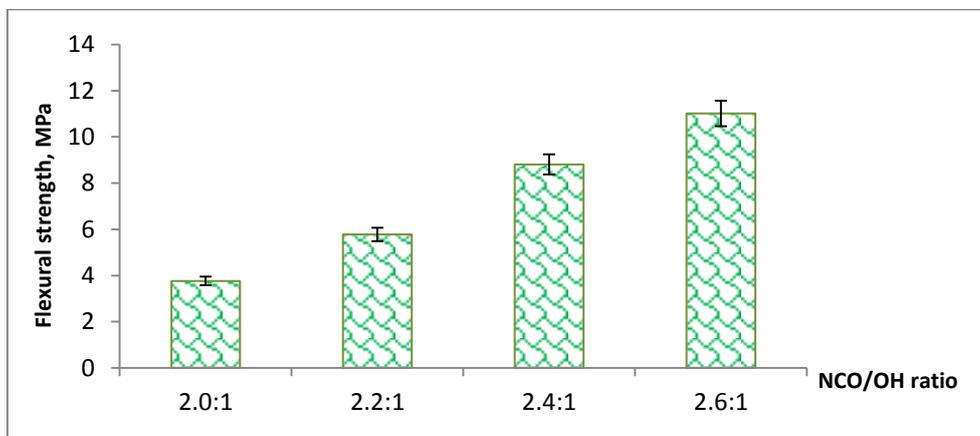


Figure 4. Flexural strength of CPUG samples.

Figure 5 and Table 2 show that the flexural modulus of CPUG samples also increased steadily with the increased of NCO/OH ratio. CPUG with NCO/OH ratio of 2.6:1 had the highest flexural modulus which was about 1069.50 MPa compared to the other CPUG samples. The increment of both flexural strength and flexural modulus of CPUG can be relate to the increased of crosslinking in CPUG which resulting an increased of CPUG's density while the density of PU grout increased proportional to the increased of NCO/OH ratio [9]. Both flexural strength and flexural modulus obtained in this research were tantamount to previous findings which stated that the flexural strength and flexural modulus of rigid PU foam increased proportionally to the increased of density of rigid PU foam [14].

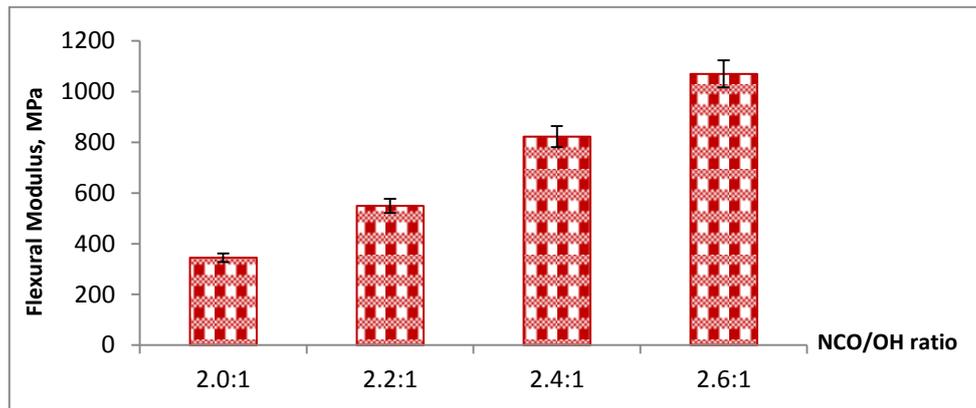


Figure 5. Flexural modulus of CPUG samples.

3.5. Compression strength

Figure 6 shows that the compression strength of CPUG samples increased with the increased of NCO/OH ratio. However, compression strength value for 2.4:1 and 2.6:1 composition remain constant at 2 Mpa indicating that CPUG samples had achieve its optimum compression strength. Apart from that, the compression strength of CPUG can be relate to the apparent density. The apparent density of CPUG samples increased with the increased of NCO/OH ratio as the hard segment content in CPUG increased which resulting an increase of crosslinking density and rigidity of CPUG. This make CPUG samples become harder to be compressed thus resulting a higher compression strength result [9]. Besides, the apparent density also increased as there was an increase of compaction arrangement of cellular structure which resulted an increased in compressive strength [15-16]. The compressive strength of CPUG was parallel to the previous studies which stated that the compressive strength obtained for PU grout having densities around 100-300kg/m³ was in range between 1-5Mpa [12].

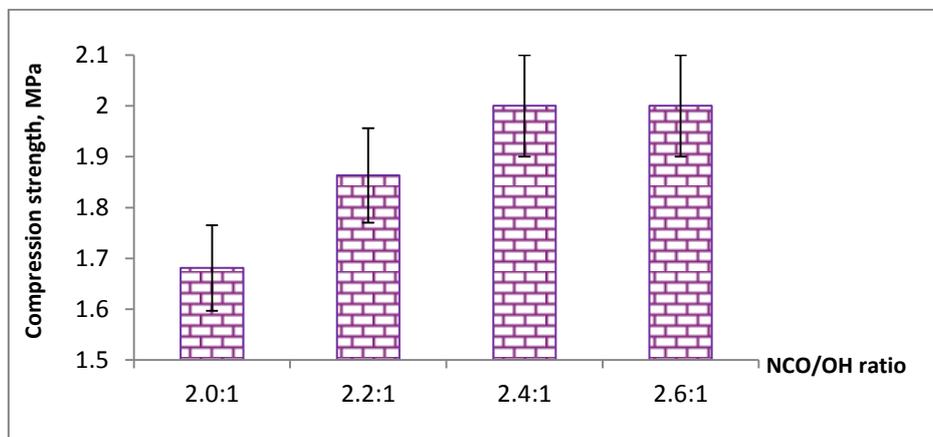


Figure 6. Compression strength of CPUG samples.

3.6. Morphological properties

Based on figure 7, CPUG samples consist of spherical and polyhedral shape of closed cell foam. The diameter of a single cell foam in four different CPUG samples decreased with the increased of NCO/OH ratio. The cell foam was produced from the exothermic reaction between polyol and isocyanate which then triggered the phase separation. The reaction caused the evaporation of blowing agent into gaseous phase and followed by diffusion of small air bubbles into the nuclei which then entrapped and resulting small size of cell foam formed in the CPUG matrix [11]. As NCO/OH ratio increased, the exothermic reaction rate increased, thus increased the amount of diffusion of air bubbles into the nuclei which resulting a decreased in cell foam size.

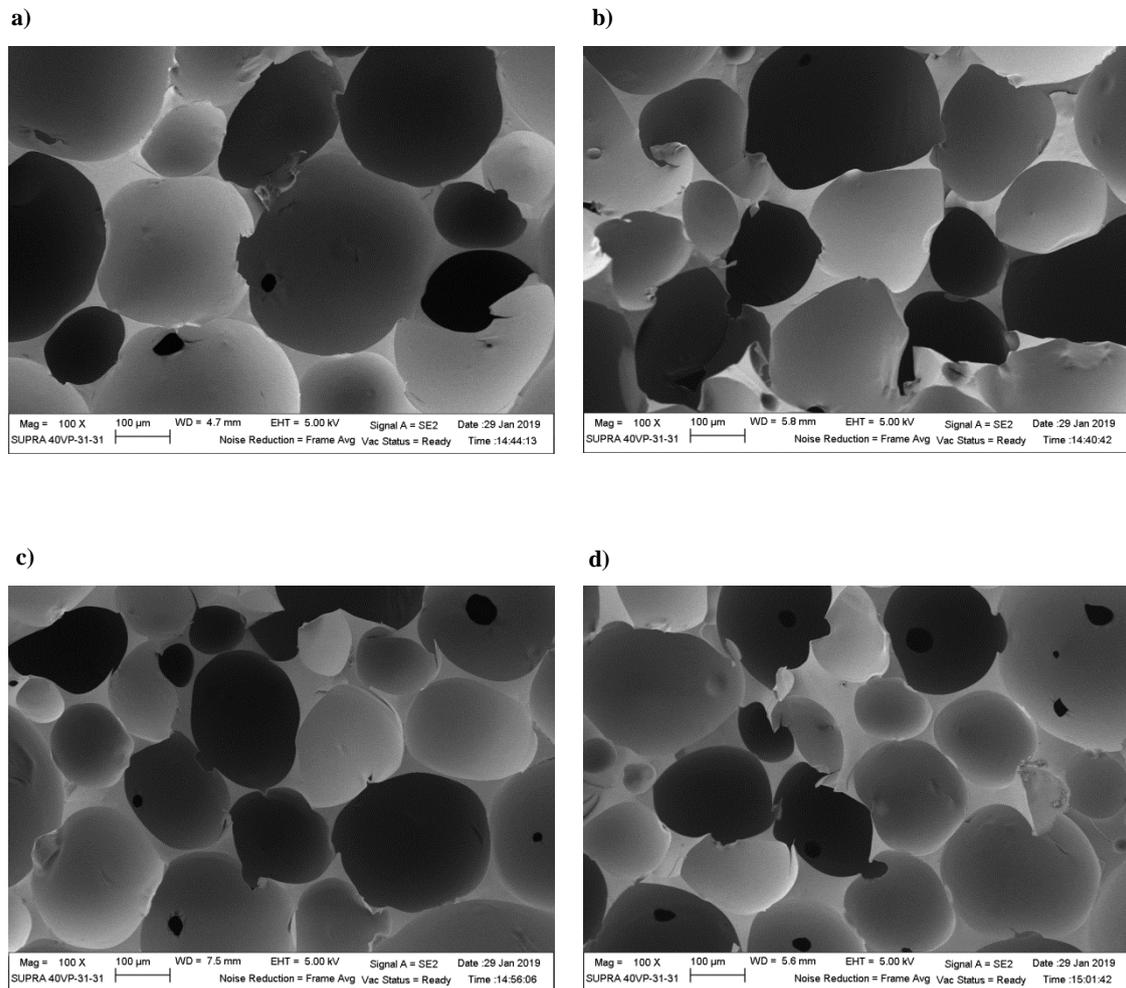


Figure 7. SEM micrograph of CPUG samples. (a) CPUG 1. (b) CPUG 2. (c) CPUG 3. (d) CPUG 4.

Apart from that, the decreased in cell foam size also caused by the decreased of cell wall's elasticity which caused by the allophanate crosslinking. These make the growth and coalescence of bubbles in CPUG become difficult and resulted a small size of cell foam. Smaller size of cell foam caused an increased of surface contact area between cell foam which resulting a more stable CPUG system [12]. Therefore, CPUG 4 had the most stable system compared to the other samples as it exhibit the smallest size of cell foam. The overall cell foam diameter of CPUG samples obtained was in range between 339 μm to 230 μm. These findings was slightly different with previous research which stated that for PU grout that had densities in range between 100-500 kg/m³, the cell foam diameter was in range between 0-150 μm [12]. The difference is possible due to different equivalent weight of castor oil and isocyanate used in this research compared to previous research.

4. Conclusions

In conclusion, the rise time of CPUG decreased while tack free time increased with the increasing NCO/OH ratio. This was due to the increased of allophanate crosslinking in CPUG samples. Apparent density of CPUG increased with the increased of NCO/OH ratio. This was due to the increased of hard segment in CPUG which enhancing the crosslinking in CPUG samples. The rheology index of CPUG increased with the increased of NCO/OH ratio as there was an increase of foaming reaction which make the CPUG samples expanding greatly. CPUG having NCO/OH ratio of 2.6:1 give the highest

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flexural strength, flexural modulus and compression strength. The increased of NCO/OH ratio caused the acceleration of foaming reaction rate of CPUG which resulting a decreased in size of cell foam.

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