DIFFERENT TYPES OF POLYOLS AND ISCOCYANATE RATIO TO THE PHYSICAL, MECHANICAL, AND MORPHOLOGICAL PROPERTIES OF POLYURETHANE

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Abstract. Due to the time-consuming preparation and hardening process of cement concrete, there has been a shift towards the use of Polyurethane as a new grouting material. This study focused on the preparation of polyurethane (PU) using two types of polyols: castor-based polyol (C) and polyether polyol (P). Five different compositions of polyurethane were created using each polyol type to investigate and compare the effect of different ratios of isocyanate and polyols on PU physical and mechanical properties. The study found that the rheology index for CPU was lower than PPU for all compositions, with an optimum value of 1.31 cm/g for CPU4 and 2.43 cm/g for PPU4, respectively. Additionally, the density of PPU was found to be higher than CPU, and both densities increased with increasing NCO ratios. Both types of samples showed a significant increase in compression strength of about 50 % compared to the lowest ratio of NCO. Overall, PPU exhibited higher compressive strength compared to CPU. The results were explained through FESEM micrographs image of the cellular arrangement of PU, which illustrated the mechanical strength of both sample types. PPU4 and CPU4 demonstrated optimum mechanical and physical properties. All results fell within the range of industrial polyurethane grouting materials, and these findings suggest that they could be used as new sources of grouting materials.

Keywords: Petrochemical polyol, castor polyol, physical properties, mechanical properties, grouting materials

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Introduction

Malaysia has one of the finest road systems in the world, stretching over 60,000 km and covering every state [1]. Malaysia uses asphalt and concrete to make pavements and roadways because it is highly durable and environmentally friendly [2]. However, many problems are faced with asphalt and concrete materials, such as unlevelled slabs, surface cracks, and holes, although many studies on road defects have been carried out overseas [3]. Polyurethane can provide repairing, sealing, void filling, and waterproofing solutions [4]. The polyurethane injection method has been proven successful as it is less hazardous and hassle. This was due to the ability of polyurethane to cure quickly, and it only takes about 2 hours for the injection process to be completely cured, allowing the road to be opened. Therefore, problems with traffic due to longer times for maintenance and high operational costs will not happen. Due to the development in the material formulation of polyurethane, there is a rising demand for polyurethane grout.

Further research is necessary to address the challenges of developing strong and rigid polyurethane grouting materials in Malaysia, as there are currently limited findings on the topic [5]. In other countries such as Japan, polyurethane grouting has been utilized to repair and reinforce earthquake-damaged underground pipelines and tunnels, while in China it has been used to stabilize soil and prevent foundation settlement during building construction [6-7]. Castor oil polyol, derived from the seeds of the castor plant, is highly reactive and able to form long-lasting, rigid polyurethane foams due to its unique chemical structure. On the other hand, vegetable oil polyol, sourced from various vegetable oils including soybean, sunflower, and canola, has a more complex chemical structure and is typically less reactive, making it suitable for use in softer and more flexible polyurethane foams [5].

The rigidity of PU is determined by the type of polyol used. The use of an isocyanate with higher functionality can result in more rigid polyurethane. Similarly, a polyol with a higher molecular weight or a higher number of hydroxyl groups can produce a more rigid polyurethane. Different types of polyols have different OH values and equivalent weights that will affect the urethane crosslinking between polyol and Isocyanate. This will influence the final properties of produced polyurethane foam. Nowadays, polyurethane production in industries commonly uses petroleum-based polyols as their main component [8]. Concerns arise on petroleum-based polyol when raw materials, such as crude oil and coal, have a rapid rise in prices, high rate of depletion, and require high technology processing system [9-10].

A new source like natural-based polyol was enforced to replace petrochemical-based polyol and overcome the problem that arises. One of it is Castor oil, a natural oil 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. Longer carbon chains typically result in polyols that have higher molecular weights and higher viscosities. This can make the resulting polyurethane foams more rigid and less flexible [11-12]. This study aims to produce rigid castor-based PU (CPU) that meets the industrial standard of grouting materials and to compare it with the properties of petrochemical-based PU(PPU). The ratio of Isocyanate to polyol for both types of PU varied in this study.

Materials and Methods

Materials

Castor oil and polypropyleneoxy sucrose are two different types of polyols that were used in this research. Castor oil has an OH value of 161.62 mg/KOH/g and an equivalent weight of 347 gmol^{-1}, while polypropyleneoxy sucrose has an OH value of 414 mg/KOH/g and an equivalent weight of 135.51 gmol^{-1}. Isocyanate used in this research is 4,4-methylene diphenyl diisocyanate with an NCO content of 31 % and a molecular weight of 360. The blowing agent used is 1,1-dichloro-1-difluoromethane supplied by Airgas USA. The surfactant used is a polyalkyleneoxide methylsiloxane copolymer manufactured by Momentive Amer Ind. Pentamethyldipropylenetriamine (PMDETA) was used as a blowing catalyst, and dimethyl cetyl hexamine (DMCHA) was used as a gelling catalyst. Both catalysts were supplied by Huntsman (Singapore) Pte Ltd.

Polyurethane Production

Table 1 illustrates the production of two types of polyurethane (PU): PPU and CPU with five different compositions that varied in isocyanate (NCO) ratios [13]. In order to create the PU, castor oil, blowing agent, surfactant, gelling catalyst and blowing catalyst were mixed in a plastic cup using a mechanical stirrer at 3000 rpm for approximately two minutes. The NCO was then added to the mixture and stirred at 3000 rpm for about 20 seconds. The samples were subsequently poured into molds and conditioned at room temperature for roughly 24 hours before being removed from the molds and undergoing post-curing at room temperature for approximately 36 hours. This process was repeated for the PPU samples as well.

Table 1: Polyurethane grouting materials formulation

Samples		Isocyanate: Polyol
Polyether Polyol (PPU)/ Castor Polyol	1	2: 1
	2	2.2: 1
	3	2.4: 1
	4	2.6: 1
	5	2.8.1

Characterization

The density of each PU sample was determined according to method BS: Part 1: 1988 Method 2, in which four PU block samples with a dimension of 50 x 50 x 50 mm from each composition were measured. The hardness test was carried out using ASTM D2240 type D durometer to penetrate the needle into the surface with 10 different points. Compression properties of PU were determined according to ASTM D 395 method B using four samples from each composition with a dimension of 50 x 50 x 50 mm and crosshead speed movement of 50 mm/min by using the Universal Testing Machine (UTM). Scanning electron microscopy (SEM) was conducted on PU samples according to ASTM E 2089 method with 100X magnification to examine the cell morphology of PU by using the JEOL JSM 6460.

A rheology test determined the capability of polyurethane to expand and flow. The test was conducted on the clear hose. The mixture of polyurethane was poured into a clear hose in the opposite gravity of the earth's direction. The hose must hold upright to ease the flow of the polyurethane resin. The sample was left to flow and expand until it hardened and stopped. The distance travelled by the flow was calculated and recorded. The rheology index of the sample was determined by using the formula below.

$$\frac{(\text{Distance of sample flow (cm)})}{([\text{weight of polyol (g)}] + [\text{weight of isocyanate (g)}])} \qquad (1)$$

All polyurethane samples with different ratios of polyol and Isocyanate of CPU and PPU are analysed using Fourier Transmittance Infrared Spectroscopy (FTIR) with a Shimadzu IR Affinity-1 instrument. This is the consequence of analysing the sample for the presence of functional groups. ASTM E1252 was employed for the FTIR analysis.

Results and Discussion

Rheology Index

The rheology index determined the ability of PU to expand and flow. Figure 1 shows the rheology index value of CPU and PPU as grouting PU.

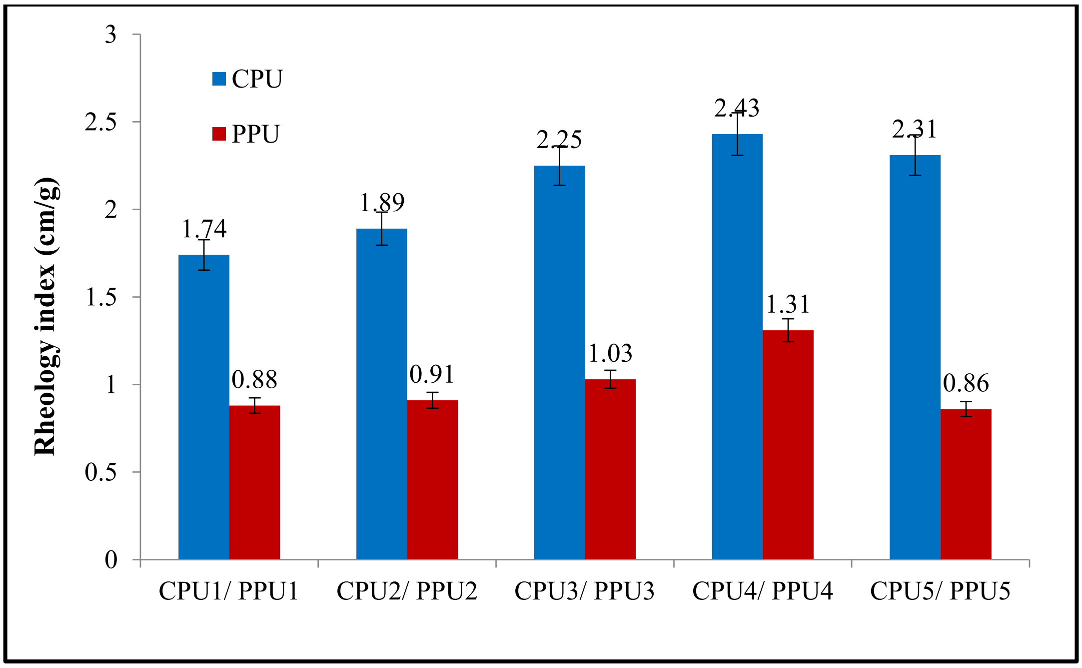

Figure 1: Rheology index of CPU and PPU

The rheology index for both types of PU increased with the NCO ratio. An increased ratio of NCO increased the interaction with OH and enhanced the foaming reaction, increasing their expandability and rheology index [11]. However, the rheology index for both types of PU decreases for a ratio of 2.8:1. Higher isocyanate amount is expected to cause an increase in the mixtures' viscosity, constricting their flow and expandability hence, resulting in the decrement in their rheology index [12]. The highest rheology index was achieved by CPU4 and PPU4, with a value of 2.43 cm/g and 1.31 cm/g, respectively.

CPU has a higher rheology index compared to PPU. A higher rheology index achieved by CPU was attributed to the lower viscosity of castor polyol compared to petrochemical-based polyol. This enables the mixture to flow at a longer distance resulting in a higher rheology index. The rheology index obtained by both types of PU is in the range between 0.4 cm/g to 5 cm/g and agrees with previous findings by [13,14] on the rheology index of industrial PU grouting.

Density Properties

Figure 2 shows the density for both types of PU. Based on Figure 2, the density of both PU increased with increasing NCO ratio. The increase of Isocyanate led to the increment of foaming reaction that resulted in higher cellular foams and a more compact arrangement of cellular foams [13]. Images of cellular foam of both types of PU as shown in the micrograph SEM image in Figure 3 [15].

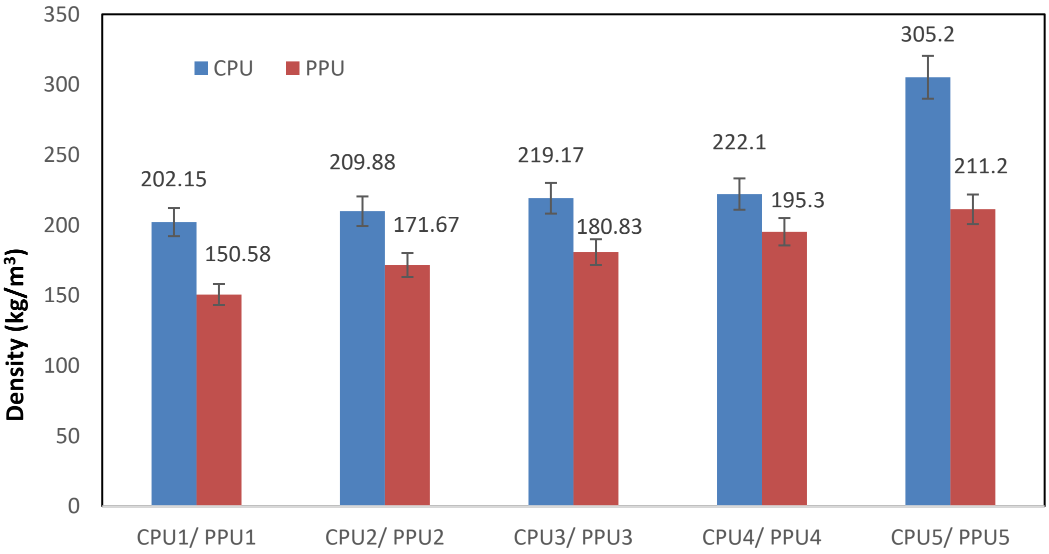

Figure 2: The density of CPU and PPU

The optimum density is achieved with an NCO ratio of 2.8 with a value of 305.20 kg/m^3 (CPU) and 211.20 kg/m^3 (PPU), respectively. Micrograph SEM in Figure 3 shows the cellular foam arrangement for CPU5 and PPU5, where it can be observed that CPU 5 contains a compact arrangement of cellular foam. At the same time, PPU 5 has the non-uniform size of the cellular foam, but a compact arrangement structure proved the density result of PU. Despite that, the results obtained for both types of PU were in parallel with commercial PU's density, which is between 90 kg/m^3 to 360 kg/m^3 [5].

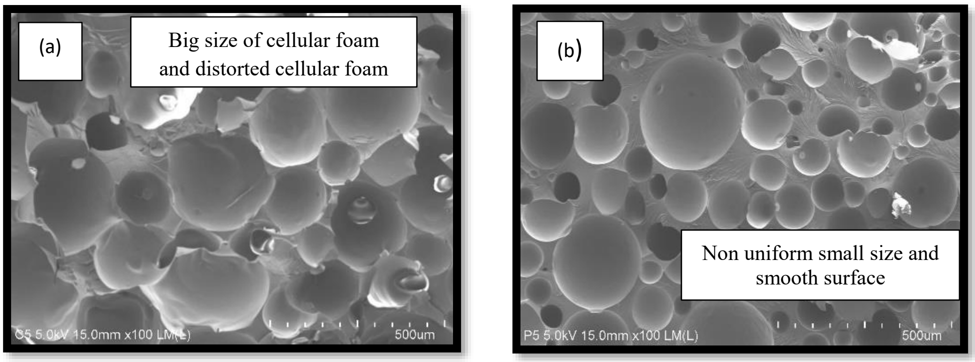

Figure 3: Cellular foam arrangement of (a) CPU5 and (b) PPU5

Hardness Properties

Figure 4 shows the hardness of both types of PU with different NCO ratios. The hardness of PU was tested using durometer type D. It can be seen that the hardness for both PU increased with increasing NCO ratio. The increase in the NCO ratio enhanced the crosslinking of urethane in the PU matrix, which led to an increase in both the density and hardness of the PU[16].

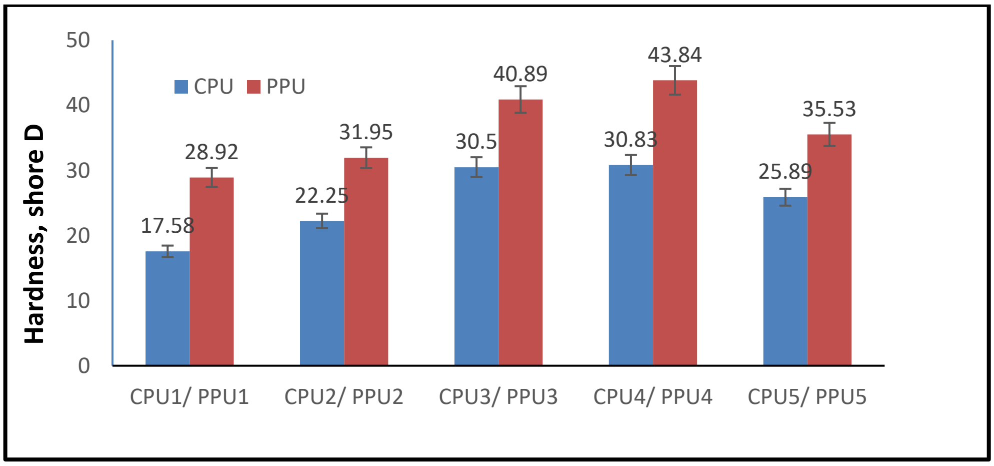

Figure 4: Hardness of PU

The hardness of both PU decreases at a ratio of 2.8: 1. This is probably due to the presence of more Isocyanate, leading to the formation of a high exothermic reaction in the PU system, which affected the foam's cellular structure [16]. The cellular foams in the PU matrix became unstable, making them easier to rupture. These caused a decrease in the hardness of PU. CPU4 and PPU4 achieve the highest hardness with a value of 30.83 shore D and 43.84 shore D.

PPU has a higher hardness compared to CPU. This is due to the higher OH functionality of petrochemical-based polyol compared to castor polyol, as shown in FTIR spectra in Figure 5. Broader peak of the OH group confirms that the petrochemical-based polyol possesses a higher OH group. The positioning of a hydroxyl group in castor polyol which is in the middle of the main chain, is an obstacle for the crosslinking to take place and leaves a long dangling chain of polyurethane [17]. These caused a plasticising effect on the CPU matrix, leading to lower hardness than PPU. The high hardness of PUG may increase their mechanical properties as the skin of the foam has a poor ability to resist pressure, making it easier to crack and debond. The hardness obtained in this research satisfactorily with commercial PU grout's hardness which is more than 20 shore D [12].

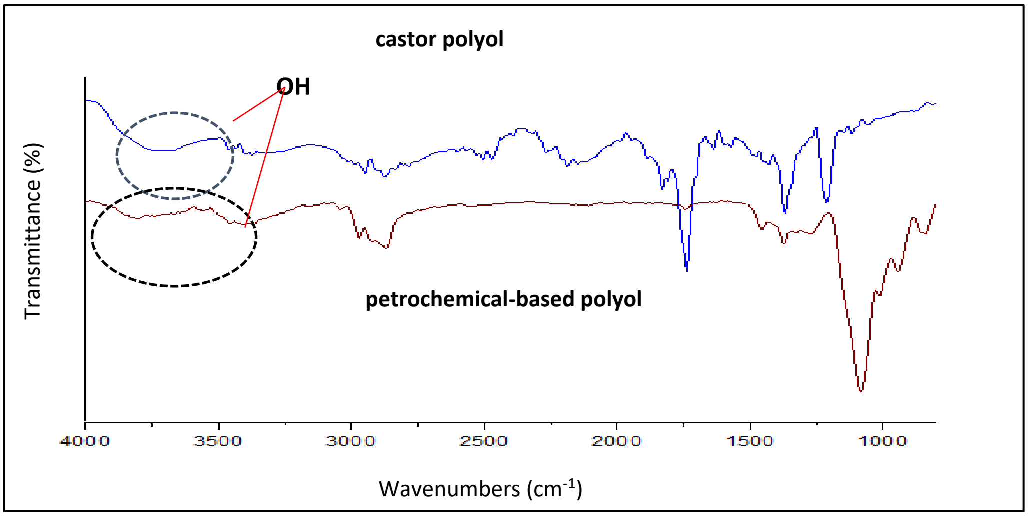

Figure 5: FTIR spectrum of two types of polyol

Compression Strength Properties

Figure 6 depicts the compressive strength of both types of PU. Compression strength refers to a material's ability to withstand a load, while compression modulus represents its resistance to elastic deformation under the applied load. According to Figure 6, the compression strength of both PU types increases with the NCO ratio except for PPU5. This finding is consistent with Sidek et al.'s previous research [18], which indicates that the compressive strength of PU foam rises as the NCO ratio increases. The increase in compression strength of both PU types is related to their density and cellular foam arrangement. The compact arrangement results in good interfacial bonding between cellular foams, with no voids between them. This enables PU to withstand high stress before failure [11]. The increase in the NCO ratio leads to an increase in urethane crosslinking, which raises the crosslinking density, making the PU more rigid and harder to compress [13].

All results obtained agreed with the previous result achieved by [20], which reported that the compression strength of PPU was in the range between 1-5 MPa and densities around 100-300 kg/m3. The compression strength of PPU is in the range of 3.19 MPa to 8.66 MPa is higher compared to CPU, where the CPU is in the range of 1.02 MPa to 3.39 MPa. The lower compression strength achieved by the CPU was due to the position of hydroxyl group in castor polyol which is in the middle of fatty acid chain. Significant steric hindrance take place when castor polyol reacted to Isocyanate due to the presence of pendant chain which also act as dangling chain, reducing the crosslinking in CPU [19]. The high OH value of petrochemical-based polyol also contributes to the increment of an exothermic reaction, which enhances the formation of more cellular foams in PPU matrix [20]. The SEM micrograph in Figure 7 shows distorted cellular foams in the CPU5 matrix observed from the FESEM micrograph of CPU5 at 100X magnification that could cause a drop of compressive strength for PPU5.

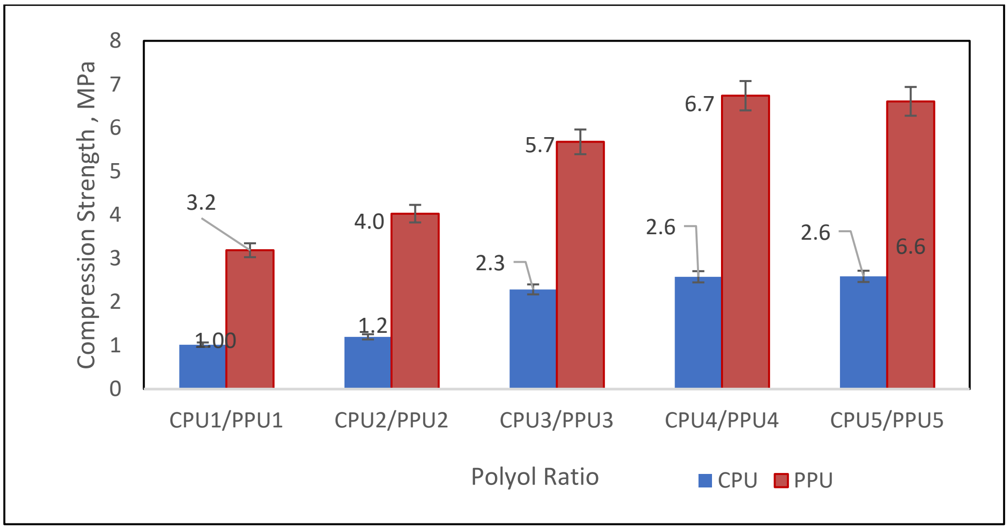

Figure 6: The compression strength of PU

Figure 8 displays the compression modulus of PPU and CPU, with PPU's compression modulus increasing as the NCO ratio rises. The same trend is seen in CPU, except for CPU 3 and CPU 5. As load is applied, yielding stress occurs, indicating the PU's ability to resist deformation. Higher yielding stress represents a higher compression modulus, indicating a greater ability of PPU to resist deformation. The increase and decrease in compression modulus of both PU types are due to increased urethane crosslinking and the formation of stable, evenly distributed, and arranged cellular foams [5]. In comparison, PPU has a higher compression modulus than CPU. Nevertheless, the results for both CPU and PPU are consistent with previous research by [20], which showed that the compression modulus attained by PU grout in their study ranged from 0.8 MPa to 12.9 MPa.

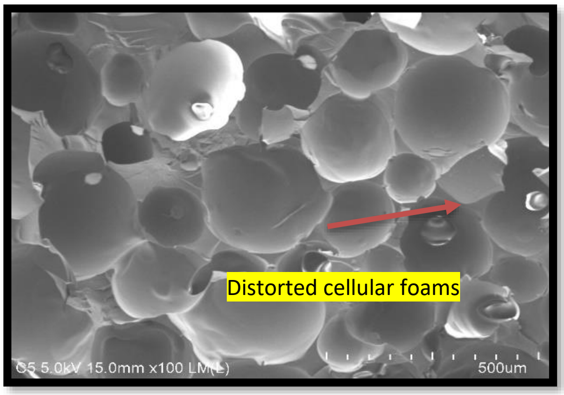

Figure 7: SEM micrograph of CPU5 Cellular foams

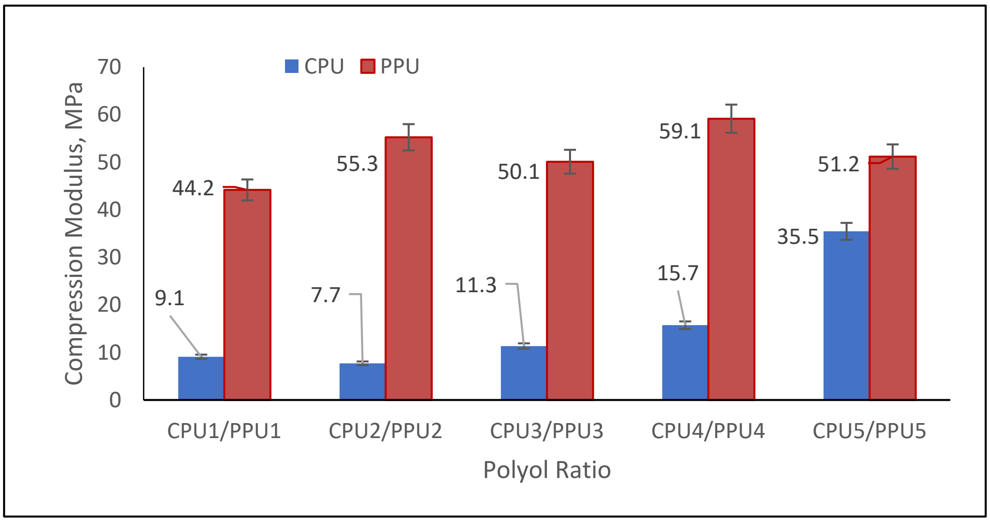

Figure 8: Compression modulus of CPU and PPU

Scanning Electron Microscope (SEM) Analysis

SEM micrographs of the CPU and PPU are displayed in Figure 9. The micrographs show that both materials are composed of closed-cell spherical and polyhedral-shaped cellular foams. PPU cells exhibited greater uniformity in size and shape compared to CPU. As the NCO ratio increases up to a 2.6:1 composition, the uniformity of cellular foam size in both CPU and PPU increases, and the cellular foam arrangement becomes more compact. CPU cellular size is bigger compared to PPU.

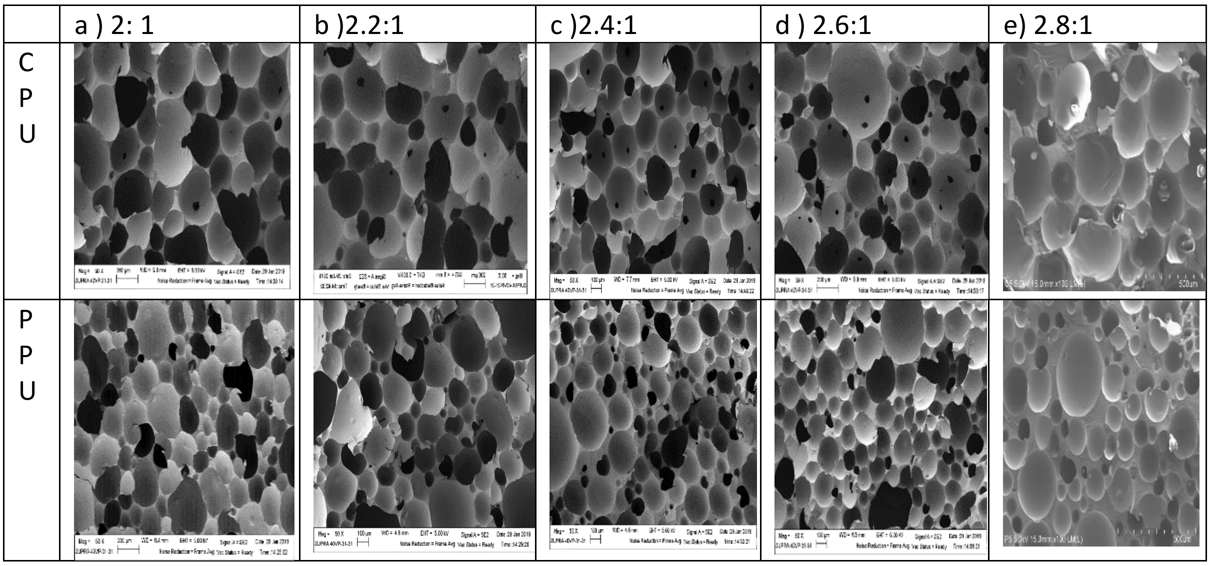

Figure 9: SEM micrographs of different types of PU at 50X magnification (a) CPU/PPU1, (b) CPU2/PPU2 (c) CPU3/PPU3 (d) CPU4/PPU4 and (e) CPU5/PPU5

However, in Figure 9(e), the cellular foams in the CPU5 matrix have distorted and irregular structures, indicating that they begin to rupture. The uneven size and rough surface of the cellular foam in all micrograph images of CPU at different ratios explain why the compression, hardness, and density of CPU are lower than PPU. The results are further explained through FESEM micrographs of the cellular arrangement of PU, which illustrate the mechanical strength of both sample types. PPU4 and CPU4 demonstrated optimum mechanical and physical properties.

Conclusions

In summary, increasing the NCO ratio led to improvements in rheology, hardness, density, and compression strength for both PPU and CPU samples. PPU4 and CPU4, with a ratio of 2.6:1, demonstrated the highest compression strength. SEM micrographs revealed a closely packed cellular foam arrangement for CPU and PPU ratio 4, which explains the high compression strength achieved by these samples. In comparison to CPU samples, PPU samples exhibited better hardness, density, and compression strength, which were within the range of industrial polyurethane grouting materials. Green polyols, such as Castor oil polyol, could also be used as polyols in the production of polyurethane as a grouting material due to their rigid properties.

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Author Contributions

All authors contributed toward data analysis, drafting and critically revising the paper and agree to be accountable for all aspects of the work.

Disclosure of Conflict of Interest

The authors have no disclosures to declare.

Compliance with Ethical Standards

The work is compliant with ethical standards

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