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Physical and Morphological Analysis of Polyurethane with Different Ratios of Polyol & Isocyanate for Grouting Applications

Fatin Nur Azmina Mohd Fauzi[1], Noor Najmi Bonnia[1,4]*, Razlan Setik[2], Azra Umairah Anuar[1] Zurianti Abd Rahman[1], Radin Siti Fazlina Nazrah Hizrin[3] and Nor Dalila Nor Affandi[3,4]
[1]School of Physics and Material Studies, Faculty of Applied Science, Universiti Teknogi MARA (UiTM) Shah Alam, Malaysia
[2]Al Fazance Resources, Block D Kelana Square, Jalan SS7/26, Petaling Jaya, Malaysia
[3]School of Industrial Technology, Faculty of Applied Science, Universiti Teknogi MARA (UiTM) Shah Alam, Malaysia
[4]Textile research Group, Faculty of Applied Science, Universiti Teknogi MARA (UiTM) Shah Alam, Malaysia
*****Corresponding author (e-mail: noornajmi@uitm.edu.my)

Malaysian infrastructure projects are experiencing a 43 % increase in the usage of polyurethane materials owing to their adaptability, long lifespan, and affordability. The mixture of polyol and isocyanate, as polyurethane (PU), possesses exceptional qualities that make it an ideal grouting material. These include being lightweight, durable and flexible, while resistant to abrasion, chemicals and weather. The primary challenges associated with the production of polyurethane are shrinkage, high absorption, and durability under high pressure due to unbalanced ratios of polyol and isocyanate. However, these challenges can be overcome using appropriate ratios. In this study, to achieve the optimum result for grouting applications, polyurethane was synthesised utilising different ratios of polyol and isocyanate (0.5:1, 1:1, and 1:0.5). The samples were tested for their physical, water absorption, and morphological properties. With a moisture absorption of less than 12 %, the product of the 1:1 ratio showed good performance in water-resistant, rigid, durable and good hydrophobicity characteristics, with a lower viscosity and weight than the other samples. In addition, the closely packed foam cells were observed in the morphology of the 1:1 ratio polyurethane sample. Through a partnership with Al Fazance Resources, polyurethane-related issues related to grouting materials used in Malaysia's construction sector may be improved.

Keywords: Polyurethane grouting; ratios; polyol & isocyanate; physical properties; morphology properties

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Infrastructure in Malaysia has undergone significant development and modernization over the years, making it one of the more advanced countries in Southeast Asia. Asphalt and concrete have been used to make pavements and roadways, but concrete was mainly used for the motorways as it is highly durable and environmentally friendly [1]. Nevertheless, pavements and motorways commonly face problems such as unlevelled slabs, surface cracks, and holes, even though many studies of road defects have been carried out [2].

Polyurethane foam has emerged as a versatile and effective material for various construction applications. The mixture of polyol and isocyanate, which produces polyurethane, has unique characteristics, such as being lightweight, tough and hydrophobic. Polyols are compounds with multiple hydroxyl [OH] groups, and are one of the main reactants used in manufacturing to provide the structural foundation for polyurethane. Polyurethane polymer networks are produced by the reaction of polyols and isocyanates [3]. Polyols enhance the physical properties of the finished polyurethane product, such as strength and flexibility. The chemical structure, molecular weight, and functionality of polyols determine their impact on various properties, including heat stability, resistance to deformation, and resilience [4]. Methylene diphenyl diisocyanate (MDI) is an isocyanate that is widely used in the manufacturing of polyurethane. The [-NCO] functional group makes isocyanates reactive by interacting with the hydroxyl groups of polyols to create urethane bonds through addition polymerization. The addition of isocyanate to polyol enhances the strength and stiffness of polyurethane. The isocyanate-to-polyol ratio significantly impacts features of the finished polyurethane such as heat stability, elasticity and hardness [5].

Different ratios of polyol and isocyanate were studied to determine the optimum formulation for concrete raising materials. Polyurethane has garnered significant interest in the field of concrete levelling, a crucial technique employed to rectify uneven concrete surfaces and address issues like settling voids and cracks

[6]. In recent years, polyurethane-based solutions have gained popularity due to their exceptional physical properties and ease of application. This study delves into the comprehensive characterization and microstructural analysis of polyurethane as a concrete levelling material, aiming to shed light on its suitability, performance and potential advantages in comparison to conventional techniques.

Currently, Malaysia requires more data on polyurethane as a grouting material [7]. The use of polyurethane in concrete levelling is relatively new compared to traditional methods like concrete replacement. Its rising popularity can be attributed to its properties such as its low viscosity, expansive nature, and high compressive strength. By injecting polyurethane foam beneath sunken or damaged concrete slabs, the material expands to fill voids and lift the structure back to its original position, offering a swift and long-lasting solution to uneven surfaces [6]. Understanding the physical properties of polyurethane foam and its behaviour within a concrete matrix is paramount to optimising its performance and ensuring its structural integrity over time [8]. Although a few studies have extensively investigated the physical and morphological characteristics of polyurethane with varying ratios of polyol and isocyanate, there is a lack of comprehensive analyses of the long-term performance and environmental effects of these materials when used for grouting applications. This is crucial for understanding polyurethane's durability and effectiveness in these applications. This gap emphasises the need for more research to confirm the practicality and long-term viability of the optimal polyurethane ratio identified in this work, regardless of changing field conditions.

This study focused on synthesising PU products from different ratios of polyol and isocyanate (hardener), and the physical and morphological properties of these products are discussed. A suitable formulation of polyol and isocyanate that produced rigid polyurethane with excellent physical and morphological properties was chosen as the best ratio for polyurethane grouting material. This research was performed in collaboration with Al Fazance Resources Sdn Bhd. Al Fazance Resources specialises in waterproofing, restoring highways and pathways, and constructing structures with grouting techniques in which polyurethane is the main ingredient.

EXPERIMENTAL

Chemicals and Materials

Polyol type NCL LG108-GI and isocyanate NCL LG108-GI were used to produce polyurethane. Both materials were supplied by Al- Fazance Resources Sdn Bhd.

Characterization Methods

Synthesis of Polyurethane

Polyurethane was synthesised by stirring isocyanate with polyol in a plastic cup using a mechanical stirrer at a speed of 3000 rpm for 5 seconds. Polyurethane was produced using 3 different ratios (0.5:1, 1:1, and 1:0.5), as shown in Table 1. After that, the samples were left for 24 hours in a plastic cup at room temperature. This was to ensure that the crosslinking process of polyurethane post curing was completed. The samples were then evaluated based on foam reaction time, rheology, density and surface morphology.

Foam Reaction Time

The foam reaction time for each sample was determined using ASTM D7487. The foaming characteristics were observed and the time was recorded when the foam rose completely and lost its tackiness. The definition of each process is listed in Table 2.

Table 1. Formulation of polyurethane.

Sample	Polyol	Isocyanate
1	0.5	1
2	1	1
3	1	0.5

Table 2. The definition of characterization time

Characterization of time	Definition
Cream time	Time taken for the mixing of the polyol and isocyanate components until the mixture began to thicken and turn to cream
Gel time	Time taken for the rising foam to begin to polymerize or gel
Rise time	Time taken for the polyurethane sample to rise and stop
Tack-free time	Time taken for the polyurethane sample to lose its stickiness

Apparent Density

The overall density of the foam, including the skin, is known as the apparent density. The formula used in determining the apparent density is given in Equation 1. The density of polyurethane can be determined according to BS: Part 1: 1988 Method 2 which involves the volume of the plastic cup used.

Rheology Testing

A rheology test determines the capability of polyurethane to expand and flow. The test was conducted in a clear hose. The polyurethane mixture was poured into the clear hose in the opposite direction of the earth's gravity. The hose was held 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 Equation 2.

Water Absorption Testing

Immersion testing is a process for measuring water absorption as per ASTM D570 guidelines. The amount of water absorbed under particular circumstances was calculated using Equation 3. Samples with dimensions of 5 cm x 5 cm x 5 cm were immersed in distilled water at room temperature for 2 hours and 24 hours. After 2 hours of immersion, the samples were drawn out, cloth-dried, and weighed. Then, immersion continued until equilibrium and a constant weight were achieved.

Scanning Electron Microscopy

The ASTM E 2089 scanning electron microscopy (SEM) method was performed at 40X and 80X magnification. An SEM model JEOL JSM 6460 was used for analysis. The specimen's cross-sectional dimensions were 10 mm × 10 mm. The shape of the foam's cells is an important aspect that defines the mechanical characteristics of polyurethane.

RESULTS AND DISCUSSION

Physical Observation Analysis

Figure 1 shows the polyurethane samples with different ratios of polyol and isocyanate after curing. After 24 hours, the samples with ratios of 1:1 and 0.5:1 became hard and rigid, while the 1:0.5 ratio sample shrank and became soft to the touch. Overall, the hard and rigid condition may be attributed to the 1:1 ratio, where all the isocyanate (-NCO) groups had reacted with all the hydroxyl (-OH) groups, resulting in the production of a fully reacted polyurethane foam [9]. During the reaction, the polyol's hydroxyl groups react with the isocyanate groups, forming urethane linkages (NHCOO-) [10], as shown in Figure 2. This balanced stoichiometry ensures that no excess unreacted polyols or isocyanates are left in the final product, which can be essential for achieving the desired properties. Due to the low water content in the 1:1 ratio sample, the foam will not shrink over time and is considered rigid [7].

$$\frac{[\mathbf{weight\ of\ polyurethane} - \mathbf{weight\ of\ cup}] \times \mathbf{1000}}{\mathbf{volume\ of\ cup}} \tag{1}$$

$$\frac{\boldsymbol{Distance\ of\ sample\ flow\ (cm)}}{[\boldsymbol{weight\ of\ polyol\ (g)}] + [\boldsymbol{weight\ of\ isocyanate\ (g)}]} \tag{2}$$

$$\frac{\boldsymbol{Wd - Wo\ (g)}}{\boldsymbol{Wo(g)}]} \times \mathbf{100} \tag{3}$$

Wd **= weight after immersion (g)**
Wo **= original weight (g)**

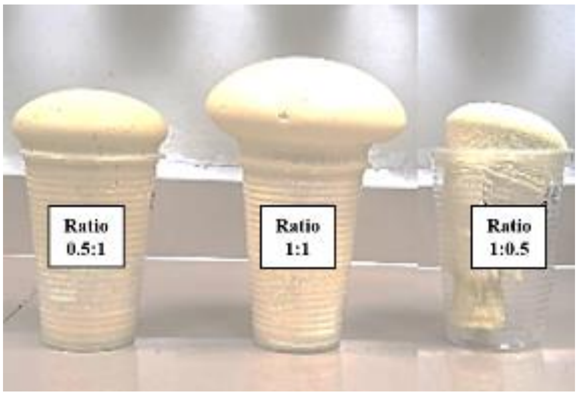

Figure 1. Polyurethane samples of all ratios after the curing process.

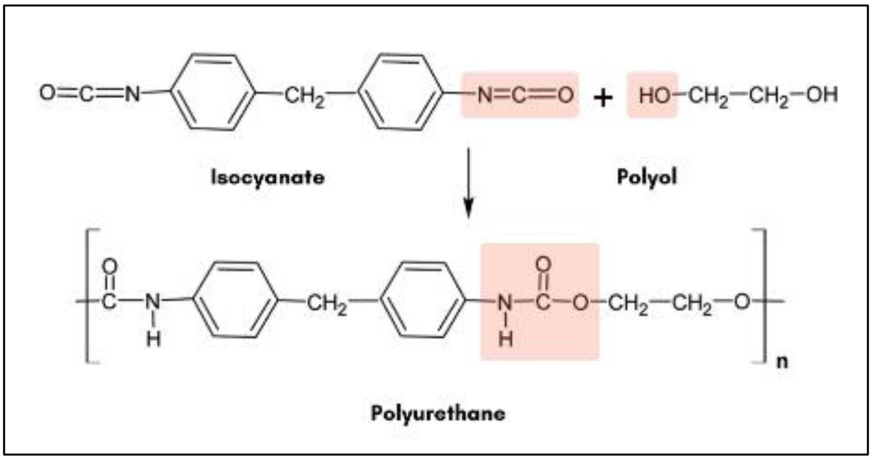

Figure 2. Chemical structure of polyurethane.

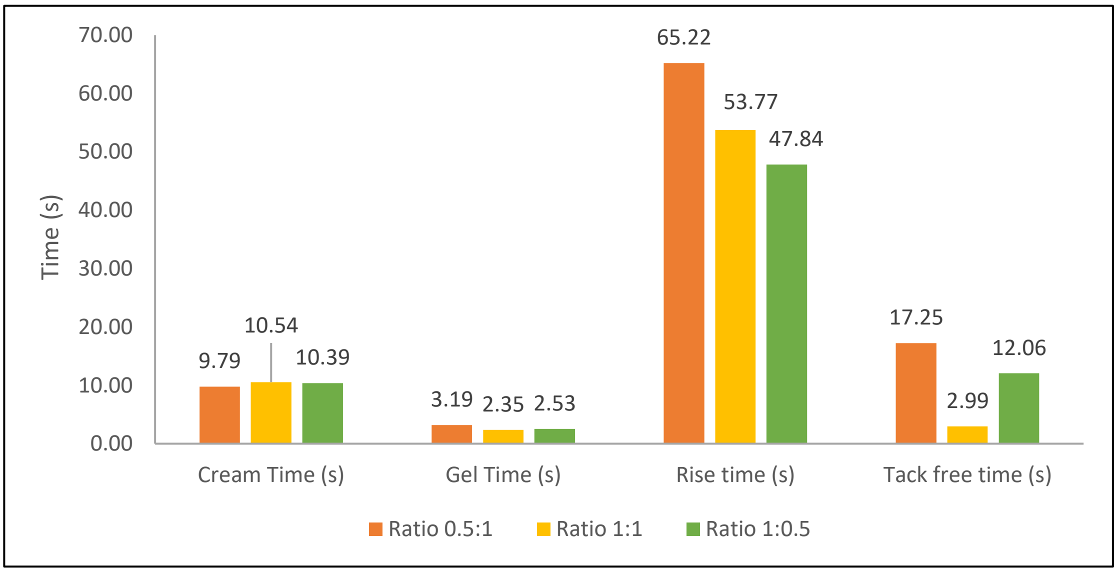

Figure 3. Foam reaction time.

Table 3. The standard foam reaction times for polyurethane grouting.

Characterization of time	Polyurethane Grouting
Cream time (s)	10-20
Gel Time (s)	Low
Rise Time (s)	>40
Tack-Free Time (s)	Low

Physical Properties of Polyurethane

Physical characterization involves assessing parameters such as time, density, and rheology. Time characterization entails measuring and recording the duration of the reaction between isocyanate and polyol during polyurethane synthesis, particularly as the mixture begins to foam.

Figure 3 illustrates the foam reaction time for the samples with ratios of 0.5:1, 1:1, and 1:0.5. The average cream time and rise time for all samples fell within the range of typical polyurethane grouting as shown in Table 3, with a cream time of 10–20 seconds and a rise time exceeding 40 seconds [11]. The amount of time taken to form the gel was low. A low gel time in the production of rigid polyurethane implies a shorter period for the material to transition from liquid to gel, enabling faster curing and production cycles. This is crucial because it marks the point where the polymerization reaction has progressed enough that the mixture starts to lose its fluidity and become solid. Notably, the tack-free times for the 0.5:1 and 1:0.5 ratio samples were considerably higher than for the 1:1 ratio sample, which averaged 2.99 seconds. This rapid loss of stickiness suggests an accelerated reaction rate [12], ensuring maximum surface protection without disruption or damage upon contact [13]. It also indicates that the surface has solidified enough to handle or move the product without marring it.

While the cream times and rise times of all samples were in line with polyurethane grouting standards, the prolonged tack-free times for the 0.5:1 and 1:0.5 ratio samples indicate they may not be suitable for concrete raising applications due to their slower reaction rates, which may potentially hinder the maintenance process [3]. Figure 11(b) reveals an excess of isocyanate in the 0.5:1 ratio and an excess of polyol in the 1:1 ratio, signifying incomplete reactions and contributing to the varying rates of reaction.

Apparent Density Analysis

The measurement of mass over volume determines the apparent density of polyurethane, which is an essential physical characteristic that may affect its strength and performance [3]. Figure 4 shows the apparent density of all the samples, which averaged 56 kg/m^3 for the 1:1 ratio, 69 kg/m^3 for the 0.5:1 ratio, and 0 kg/m^3 for the 1:0.5 ratio. These different values showcase the distinct properties and performance characteristics of each polyurethane sample. [14].

The high density of polyurethane is directly related to crosslinking and foam rigidity, as a high isocyanate content in polyurethane leads to an increase in hard segments [10]. Unreacted isocyanates can contribute to the material's reactivity, leading to potential issues with curing and crosslinking. These unreacted isocyanates remain chemically active and can potentially react with other molecules in the material or the surrounding environment. Crosslinking refers to the formation of bonds between polymer chains that create a three-dimensional network structure. The rise of hard segments (-NCO) leads to the production of extensive urethane and allophanate crosslinking in the sample, which increases the density of the polyurethane [15]. Allophanate crosslinking, as shown in Figure 5, is a side reaction that happens when unbound isocyanate or unreacted NCO groups in a polyurethane sample react with the urethane form [16]. The denser network results in a higher density material. High-density polyurethane shows brittle characteristics compared to low-density polyurethane, which exhibits elastoplastic characteristics [14]. As illustrated in the SEM images in Figure 6, cell rupture occurs between the cells, making polyurethane easy to permanently deform under stress.

The apparent density value for the 1:0.5 ratio sample was not calculated due to the shrinkage problem, and the physical properties of this polyurethane which was too soft. The presence of excess hydroxyl groups may increase the material's hydrophilicity or susceptibility to moisture absorption because it has voids in the cell structure, as shown in the SEM images in Figure 6 [18]. These can lead to issues such as reduced mechanical strength, dimensional instability, and increased vulnerability to degradation. With excess polyol, the density of crosslinking and the polymer network may be reduced, resulting in a less rigid or less durable material compared to a stoichiometric product [17].

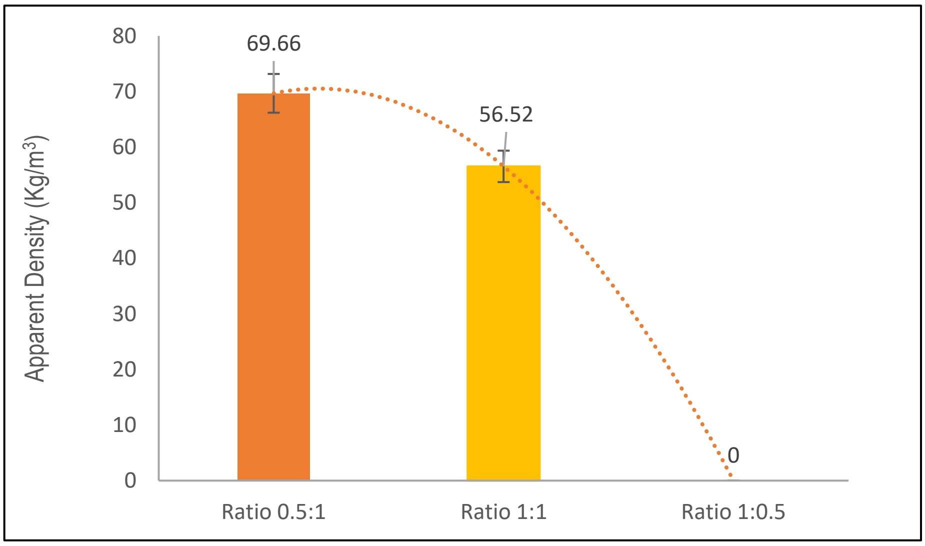

Figure 4. Apparent density of PU products of all ratios.

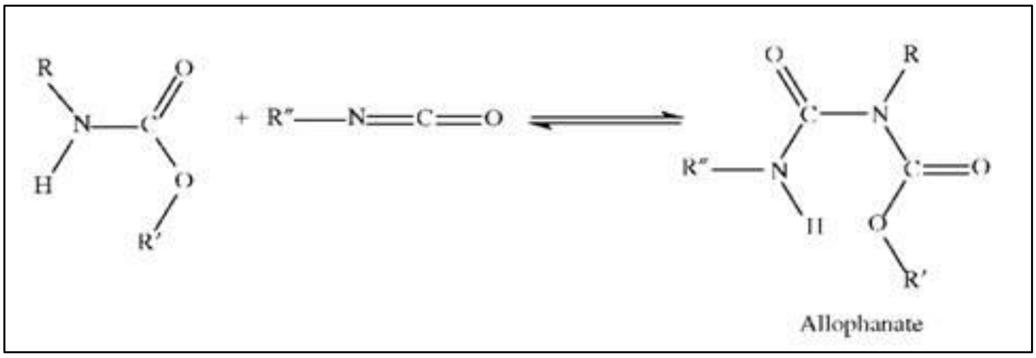

Figure 5. Allophanate crosslinking

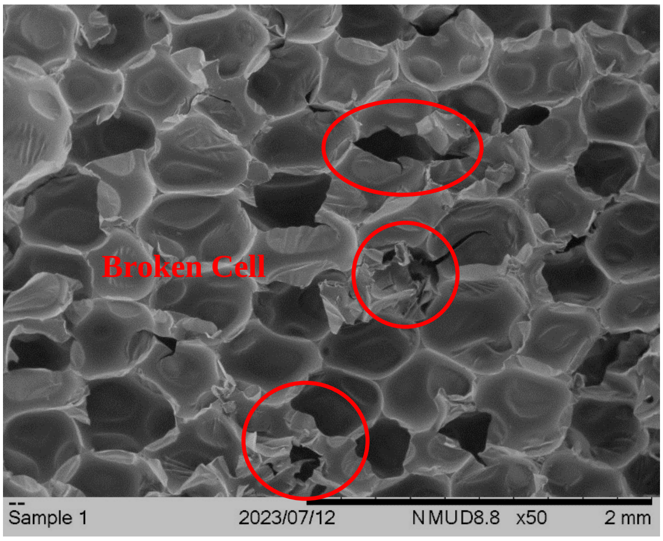

Figure 6. Microscopy image of ratio 0.5:1.

Rheology Index Analysis

The rheology index indicates the viscosity of polyurethane by observing its ability to expand and flow into cracks in pavements or concrete bridges. The further the distance travelled, the higher the rheology index and the lower its viscosity, making the material suitable for injection into cracks or potholes [19]. Viscosity measures how internal friction affects the movement of polyurethane grouting through a medium [20]. Low viscosity indicates low resistance, easy shearing, rapid flow, and a greater ability to expand and flow. This is advantageous in applications like injection moulding, where precise filling of moulds is essential for achieving desired part dimensions and properties.

The rheology index of polyurethane grout is between 0.4 cm/g and 5.0 cm/g. Based on Figure 7, all the samples were within the range required for polyurethane grout. The 1:1 ratio sample had a lower viscosity than the others because it had a higher rheology index [20]. Low viscosity is essential to the properties of polyurethane grout [21], and in this case, the 1:1 ratio sample was suitable for polyurethane grout. The 0.5:1 ratio sample that had a higher content of isocyanate produced polyurethane that was smaller in volume due to less expansion, and became brittle after curing [20]. Additional isocyanates may increase the polymer chain’s mobility, potentially reducing its viscosity.

The 1:0.5 ratio sample had the highest viscosity of all. This may be due to the high content of polyol in the polyurethane product that shrunk in the hose after a day, as shown in Figure 8. Introducing extra polyol into the reaction potentially enhances hydrogen bonding interactions within the polymer matrix. This increase in the interactions between molecules elevates its viscosity, making the material more resistant to flow. Despite the 1:0.5 ratio sample achieving a travel distance of 56 cm, its high viscosity rendered it unsuitable for use as polyurethane grouting. [19].

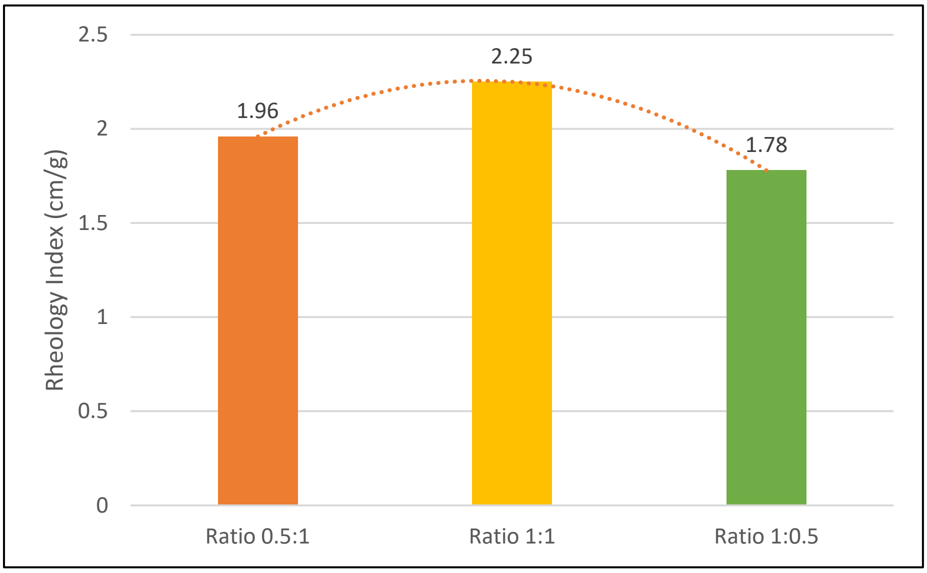

Figure 7. Rheology index values for polyurethane of all ratios.

Figure 8. 3 samples of shrunken polyurethane with a ratio of 1:0.5 in the hose.

Water Absorption Analysis

Water absorption analysis is essential for determining whether the polyurethane sample exhibits hydrophobic or hydrophilic properties. Figure 9 depicts the weight gain percentage when samples were immersed in distilled water without being subjected to pressure. When polyurethane foam encounters water, diffusion of water into the foam is observed.

Overall, the 1:1 ratio sample showed an increased weight percentage but it remained within the acceptable range for grouting PU, thus water absorption did not exceed 12 %. This ratio had the lowest average percentage of weight gain compared to the others. This was proven by the surface morphology images depicted in Figure 12(a), which showed no intercellular spaces in the structure, making water diffusion difficult [23]. The closely packed arrangement of the cells renders the sample hydrophobic, which almost repels water. This occurs because there is a greater surface area available for the diffusion of the substance, but a comparatively smaller surface area through which the substance can enter the cell.

For the 0.5:1 ratio sample, the water absorption percentage increased and continued to rise until day 15. The highest percentage of weight gain was 29 %, and the lowest was 7.2 %. This indicates that water diffused into the sample, making equilibrium difficult to achieve [24]. The tendency of high-density substances to sink instead of float in water allows them to absorb water easily. Figure 10 illustrates how a higher crosslinking density in polyurethane can diminish water absorption by restricting the movement of polymer chains and impeding the diffusion of water molecules into the material [25].

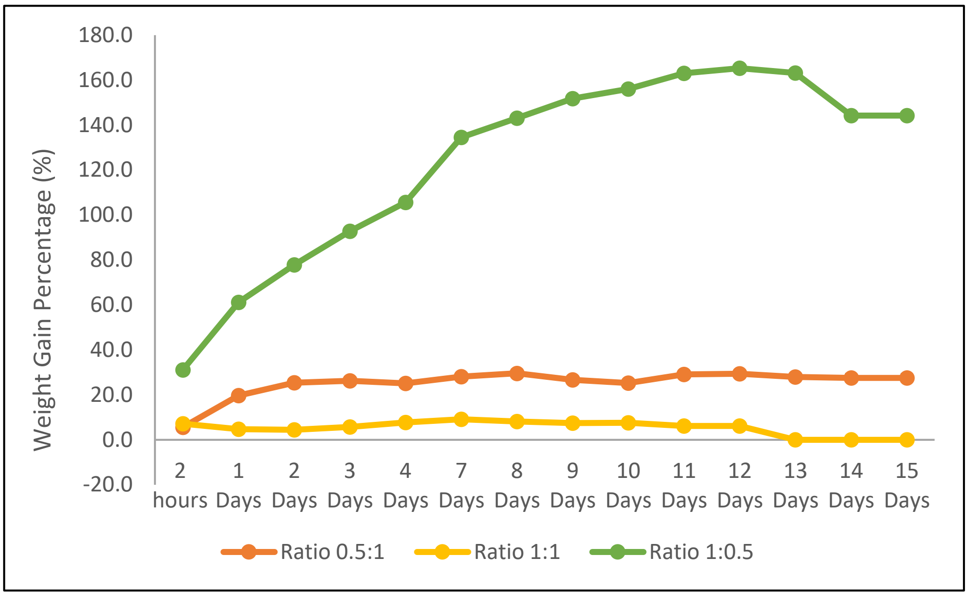

Figure 9. Weight gain percentages for polyurethane of all ratios.

Lastly, in the 1:0.5 ratio sample, the water absorption percentage rose for 12 days before decreasing slightly on day 13 although continuing to absorb water. The highest it achieved was 165 %. This indicates that the material has more capillaries or is more porous, resulting in greater water absorption and increased weight [26]. The microscopic image in Figure 12(e) demonstrates this, showing holes in each cell wall, which allows water to diffuse in, spread throughout the sample and cause it to swell. Therefore, a 1:05 ratio of polyurethane did not meet the requirements for a grouting material due to its porous characteristics.

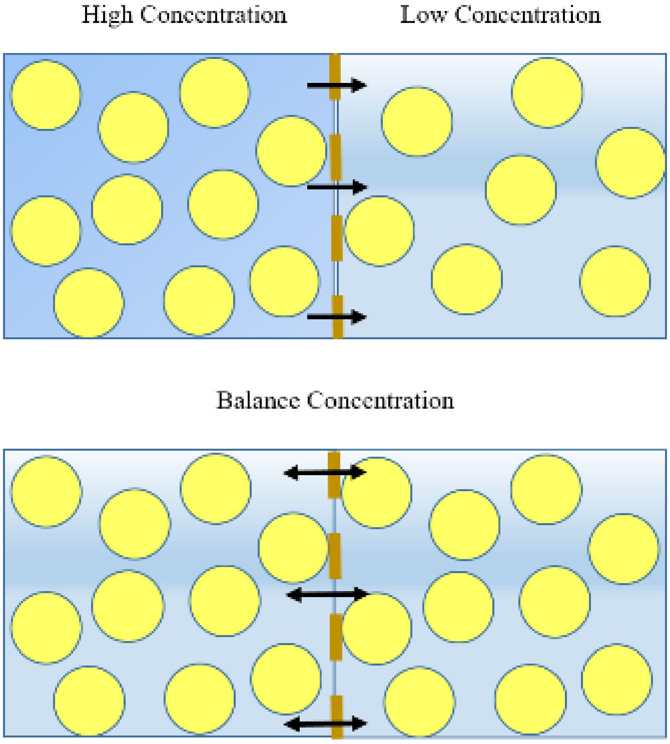

Figure 10. Diffusion of water into polyurethane.

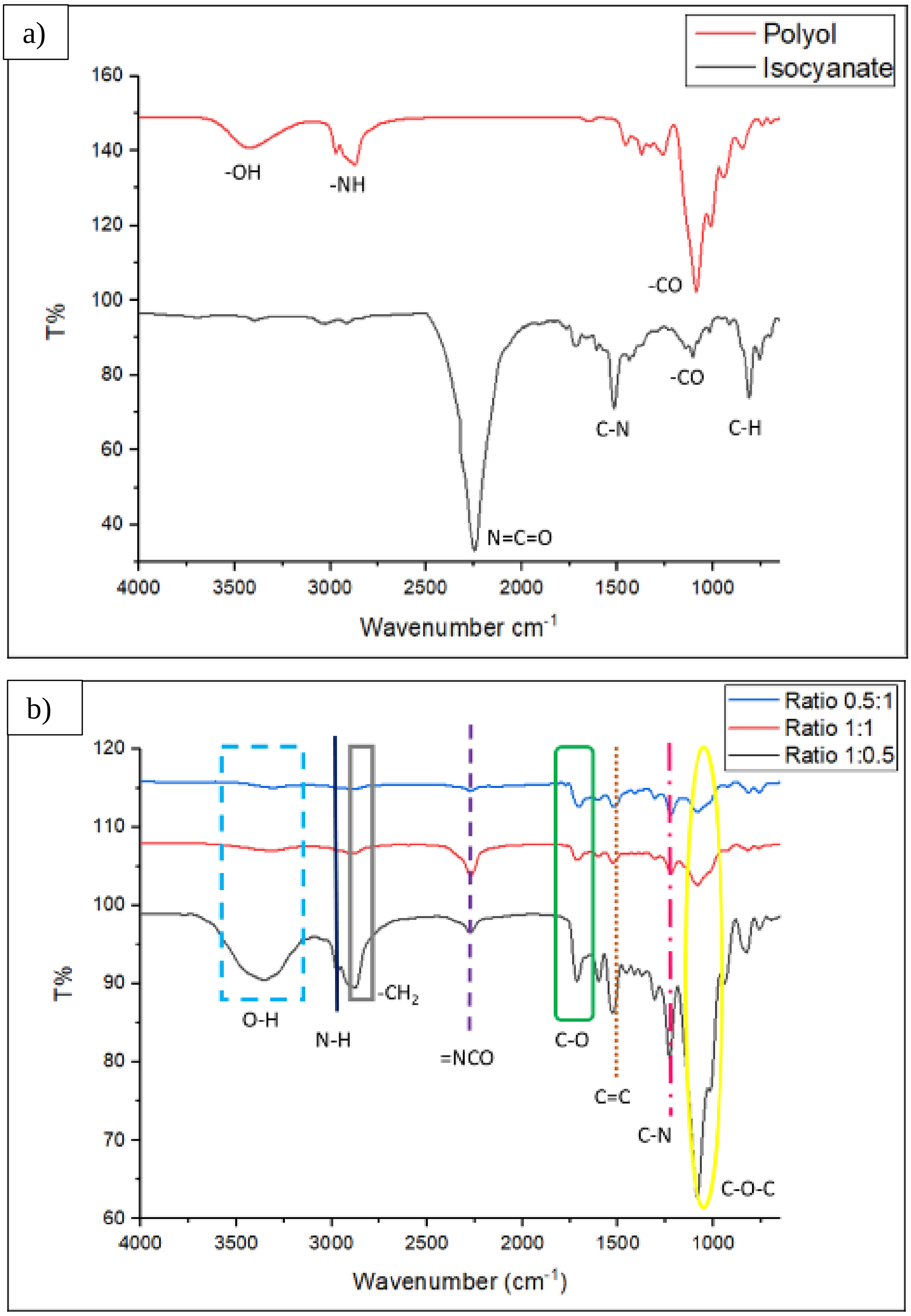

Figure 11. (a) FTIR spectra of polyol and isocyanate; (b) FTIR spectra of polyurethane of different ratios

FTIR Analysis of Polyurethane

FTIR was used to analyse the chemical structure and interactions between the polyols and isocyanates in polyurethane. The FTIR peaks correspond to the functional groups present in the samples. The spectra of raw polyol and isocyanate are presented in Figure 11(a). The spectrum of polyol exhibits absorption bands within the range of 3500 to 3200 cm^{-1}, which correspond to the stretching of O-H functional groups. The isocyanate groups were identified by the bands at 2250 cm^{-1}, which correspond to the stretching of -N-C-O- bonds.

A comparison of the spectra of the three samples is presented in Figure 11(b). The spectrum of the 1:1 ratio sample shows the presence of polyol and isocyanate functional groups that correspond to the C=O, CN-H and C-O-C at 1700 cm^{-1}, 1660 cm^{-1} and 1200 cm^{-1}, respectively, which are almost identical to the peaks in the spectra of raw polyol and isocyanate. This shows the material has a highly cross-linked structure containing a much higher proportion of urethane and substituted urea groups, which induces strong hydrogen bonding exchange forces (non-covalent interactions) [27]. In addition, the infrared spectra of the polyurethane samples with ratios of 1:1 and 0.5:1 displayed smaller and broader bands than the sample with a ratio of 1:0.5, indicating that there was no excess polyol in the samples and all of the isocyanates in the pre-polymer had reacted with each other [27]. Furthermore, the C-O-C stretching peaks exhibited a greater intensity compared to the other samples. This can be attributed to the presence of excess polyol in the polyurethane formulation with a ratio of 1:0.5.

The isocyanate (-N-C-O-) content of the 1:0.5 ratio sample was lower than other samples, indicating that this ratio contained a higher composition of polyol, causing the sample to shrink throughout the curing process, as seen in Figure 1. Thus, polyurethane with a 1:1 ratio comprised all functional groups that constituted a well-made polyurethane. Excess polyol in the 1:0.5 ratio sample reduced its tendency to form urethane linkages [17]. Fewer urethane bonds were formed with a lower isocyanate concentration in the polyurethane system, resulting in a weaker interaction between polyurethane chain molecules.

Morphology Analysis of Polyurethane

Figure 12 displays SEM images of the cross-sections of the three polyurethane samples at magnifications of 80X. This approach was employed to observe the standard rigid and flexible polyurethane foam cell structures [28].

Figure 12(a) shows that the cell structure of the polyurethane material exhibited uniform and consistent cell sizes, with no cracks evident. The uniformity of cell size and regularity of arrangement enhanced its mechanical properties. The low-density feature of the 1:1 ratio sample signified that the material was both lightweight and extremely efficient in terms of its performance-to-weight ratio [28].

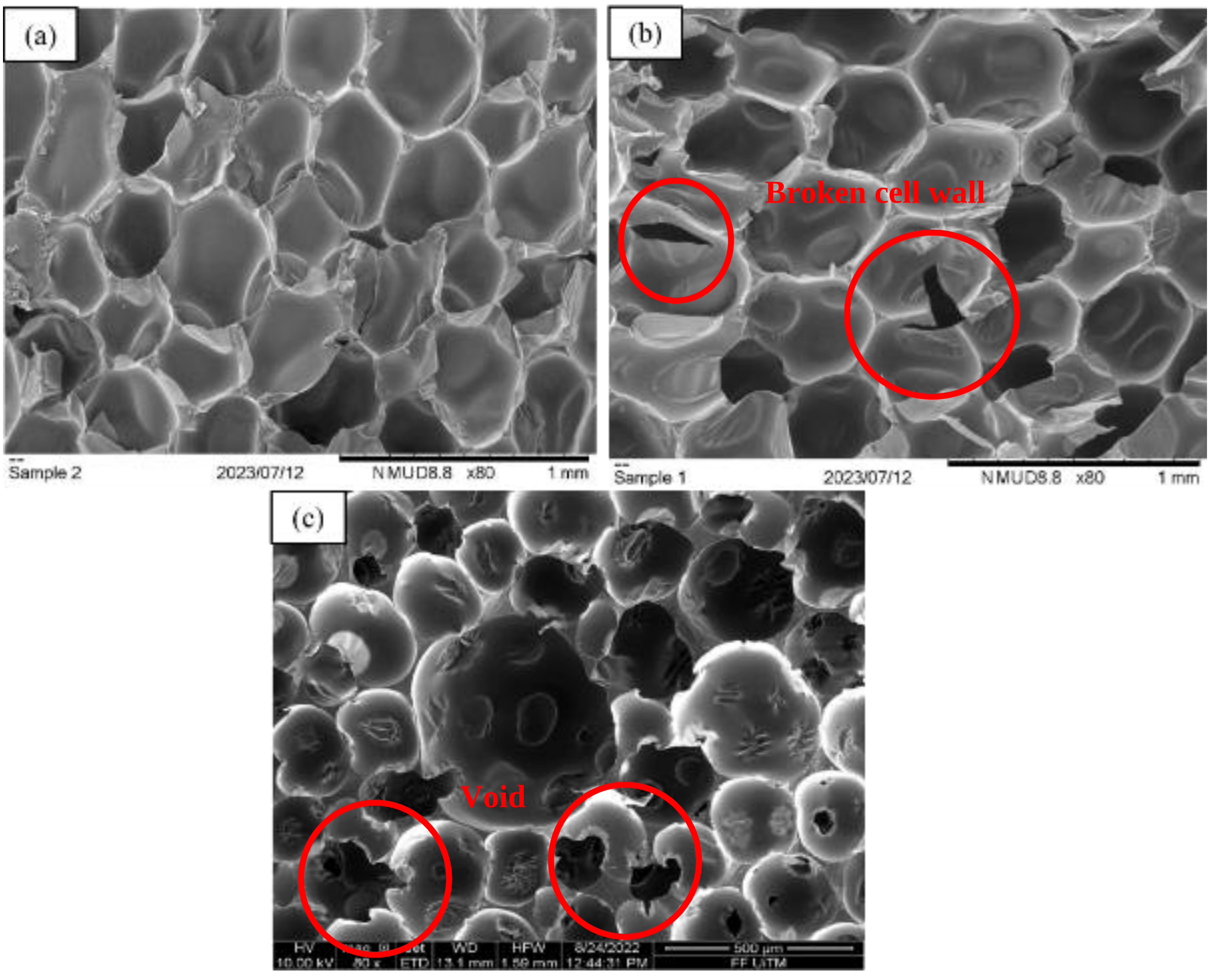

Figure 12. Microscopic images of PU samples with a (a) 1:1 ratio, (b) 0.5:1 ratio, and (c) 1:0.5 ratio.

Figure 12(b) illustrates that the foam had a nearly uniform cell size and several broken cell walls. The different cell arrangement increases the likelihood of defects. Irregularities or significant variations in cell size can create weak points in the foam, leading to reduced strength and a higher likelihood of failure under stress [21]. The damaged foam within the cell structure demonstrated its brittle and dense characteristics, as seen in Figure 6. Moreover, microscopic data showed that the cell walls may not be able to handle excessive loads. In the absence of applied pressure, the structure of the sample cell exhibited the formation of several cracks, which can be classified as brittle fractures or failures [29]. Therefore, the SEM images demonstrate that brittleness and plastic failure can result from high-density polyurethane.

A structure with a high polyol content has fewer cells and larger cell sizes, with holes or tears in each cell foam, as shown in Figure 12(c). This demonstrates that the 1:0.5 ratio sample with high viscosity, as shown in Figure 7, inhibited cell expansion. These microscopic images reveal that an increase in polyol caused a greater number of cells to open with a smaller size, resulting in a denser foam but poor interfacial adhesion between the polyol and isocyanate due to agglomeration in the polyurethane foam matrix [29]. As illustrated in Figure 12(c), a decrease in the isocyanate index produced more open-cell structures with somewhat larger cell sizes at the expense of increased irregularities. This outcome was consistent with the well-established behaviour of flexible polyurethane foams [30].

CONCLUSION

Polyurethane samples were successfully synthesised using three different ratios of polyol and isocyanate. The 1:1 ratio sample exhibited excellent characteristics in terms of characterization time, density, rheology and water uptake, compared to the 0.5:1 and 1:0.5 ratio samples. The 1:1 ratio sample had good hardness and rigidity, and was well-suited as a polyurethane grouting material. FTIR analysis indicated that the this sample possessed more complete urethane linkages than the others. Water absorption of the 1:1 ratio sample was 7.2 %, demonstrating its suitability as a grouting material, which was supported by microscopic images revealing its uniform cell size and arrangement.

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