

A Comparative Analysis of the Physical, Mechanical, and Morphological Properties of Industrial vs. Green Polyurethane as Grouting Materials

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Abstract

Polyurethane has become an essential material in the construction industry, particularly in grouting applications, due to its strong adhesive and sealing properties. Traditionally, industrial polyurethanes derived from petrochemical sources have been widely used. However, the current formulation in production of polyurethane suffers from semantic ambiguity and inconsistent terminology also growing environmental concerns have prompted to develop of greener alternatives made from renewable sources. This study compares the physical, mechanical, and morphological properties of 3 types of polyurethane: industrial polyurethanes (PI), castor oil PU with 1,1-dichloro-1-fluoroethane (HCFC 141b) blowing agent (PCH), and castor oil PU polyurethanes with water as the blowing agent (PCW). The foam reaction times of all types of polyurethane met standard benchmarks for grouting materials, with cream times ranging from 10 to 20 s and rise times exceeding 48 s. The PCW exhibited the lowest apparent density while maintaining significant mechanical strength compared to PI. All polyurethane samples demonstrated compression strengths and moduli above the standard values for grouting materials (compression strength: 30 - 150 kPa; modulus: 150 - 500 kPa). Fourier Transform Infrared Spectroscopy (FTIR) analysis confirmed completed curing process across all samples, with the expected including N-H, C=O and C-O stretches, as well as C-N stretches associated with the urethane linkage. Morphological analysis revealed a uniform cell structure in all types, despite variations in cell size, resulting in no gaps between cells. PCW has the best cell arrangement after compress as the size of the remain the same, contributing to their strong mechanical performance. This study identifies green polyurethane (castor oil) with water as the blowing agent can offering superior performance for the grouting industry, presenting it as a viable replacement material with reduced environmental impact.

Keywords: Industry polyurethane, Green polyurethane, Blowing agents, Grouting applications, Physical properties, Mechanical properties, Morphology analysis

Introduction

Polyurethane has become one of the most widely used polymers in the modern world, known for its versatility, durability, and adaptability across a wide range of industries. Its applications span from construction and insulation to automotive and consumer goods, and its usage continues to grow due to its unique properties [1]. One specific and highly significant use of

polyurethane is in grouting, a technique employed to fill cracks, stabilize soils, and prevent water infiltration in infra structure projects. The traditional industrial polyurethanes are synthesized from petrochemical resources, which, while effective, raise concerns due to their environmental impact, particularly their nonrenewable nature and potential for pollution. In

response to these issues, green polyurethanes, which are derived from renewable resources such as castor oil, have been developed. These green alternatives aim to reduce the carbon footprint of polyurethane production while maintaining or even enhancing the material's performance in various applications, including grouting [2].

Castor oil is a vegetable oil derived from the seeds of the *Ricinus communis* plant. Known for its unique chemical composition, it is rich in ricinoleic acid, a rare hydroxyl fatty acid that gives castor oil its distinctive properties, including high viscosity, stability, and moisture retention [3]. Castor oil has gained increasing importance in the construction industry due to its sustainable and versatile nature, particularly in the development of bio-based polyurethanes, coatings, and sealants. In the production of polyurethane from castor oil, the incorporation of a blowing agent is crucial. It facilitates the formation of a foam structure, reduces the overall density, enhances thermal and acoustic insulation, improves mechanical flexibility and cushioning properties, and enables greater volume expansion using less raw material. The most used blowing agent for castor oil-based polyurethane is HCFC-141b. However, its use raises environmental concerns due to its ozone-depleting potential and contribution to global warming, as well as the release of toxic by-products during degradation. Furthermore, the biodegradability and lower toxicity of castor oil contribute to safer handling and reduced environmental impact compared to conventional synthetic polyurethanes [4].

To address these environmental concerns, it is essential to explore alternative blowing agents that are non-toxic, environmentally friendly, and sustainable. The development of green blowing agents is crucial to minimizing ecological impact and ensure safer polyurethane production. Water is considered one of the most natural and environmentally friendly candidates for use as a blowing agent. In this study, the mechanical, physical, and morphological properties of castor oil-based polyurethane produced using 2 different types of blowing agents will be investigated and discussed. Two blowing agents were utilized are 1,1-Dichloro-1-fluoroethane (HCFH 141b) and water. A blowing agent is a chemical substance utilized in the production of polyurethane foam to produce gas, which forms the

cellular structure of the foam [5]. The gas expansion process occurs via physical or chemical mechanisms. Physical blowing agents are volatile liquids such as HCFC-141b that vaporize upon heating, leading to the expansion of the polymer matrix. In contrast, chemical blowing agents are substances, such as water, that when undergo chemical reactions it will generate gases like CO₂ [6].

Unlike other physical blowing agents, HCFC-141b offers superior thermal insulation, making it ideal for applications such as refrigeration and construction, where energy efficiency is crucial. Its excellent solubility in polyols promotes uniform foam structure and enhances compatibility with PU systems, minimizing defects during manufacturing. Furthermore, the relatively low boiling point of HCFC-141b facilitates efficient foam expansion under standard production conditions, leading to consistent cell size and mechanical properties [7]. Water is a popular blowing agent for polyurethane (PU) foam due to its environmental and economic benefits. Water as a blowing agent makes PU foam production more sustainable, supporting global environmental policies like the Montreal Protocol and Kyoto Protocol 9 [8]. Water is cheap, abundant, and easy to handle, making it a cost effective option for manufacturers. Water-based foaming provides a strong cellular structure, enhancing mechanical and thermal qualities for insulation, automotive, and construction applications [9].

The grouting industry requires materials that offer high mechanical strength, durability, and resistance to environmental factors such as moisture and temperature fluctuations [10]. This study compares industrial and green polyurethanes based on these requirements, focusing on their physical, mechanical, and morphological properties. By evaluating these properties, the study seeks to provide a comprehensive understanding of the potential of green polyurethanes to replace or complement industrial polyurethanes in the grouting.

Materials and methods

Chemicals and materials

The industrial polyurethane, materials used in the production are Polyol type NCL LG108-GI and NCL LG108-GI isocyanate. Both materials are supplied by Al Fazance Resources. As for the green polyurethane the

chemicals used were castor oil based polyol contain of hydroxyl value if 161.89 g/mol. Isocyanate (4,4-methylenediphenyl diisocyanate) with NCO content: 31%, molecular weight: 360, Pentamethyldipropylenatriamine copolymer

(PMDETA) function as blowing catalyst and dimethylcetylhexamine (DMCHA) function as gelling catalyst where both catalysts were supplied by Teguh Sainstek Sdn Bhd. Water (H₂O) and 1,1-Dichloro-1-fluoroethane (HCFC 141b) will be act as blowing agent.

Table 1 Characterization of the materials in this research.

Material	Appearance	Equivalent weight (g/mol)	Comments
NCL LG108-GI Polyol	Yellowish	-	OH value : 199 mg KOH/g
Castor oil	Pale yellow viscous	933.45	OH value : 161.68 mg KOH/g
NCL LG108-GI Isocyanate	Dark brown	-	Viscosity : 200
4,4-methylenediphenyl diisocyanate	Dark brown	360	NCO content : 31%
HCFC-141b	Clear colourless	-	Physical lowing agent
Distilled water	Clear colourless	18.02	Chemical blowing agent

Fabrications of polyurethane

Polyurethane was synthesized using in situ method by stirring hardener (isocyanate) with polyol in a plastic cup using a mechanical stirrer at a speed of 3,000 rpm for 5 s with ratio 1:1. After that, the sample was left for 24 h in a plastic cup at room temperature for post curing process. This is to ensure that the crosslinking process of polyurethane for was completed. The steps were repeated 3 times in order to achieve precision and accuracy. For the production of green polyurethane, the ratio of polyol and isocyanate were ratio 1:1 same as

industry based polyurethane. The castor oil based polyol (PCW) were mixed with water as blowing agent before introduced hardener (MDI) and stirred for 5 s at 3,000 rpm using the mechanical stirrer. The sample then rest for 24 h at room temperature for curing. **Table 2** shows the chemical composition of the polyurethane sample, industry based polyol and castor oil polyol with HCFC 141b and water as blowing agent. **Figure 1** shows the schematic diagram of the steps involved in fabrication of polyurethane.

Table 2 Ratio of the polyol to isocyanate polyurethane from Industry based Polyol and polyol to isocyanate to blowing agent for castor oil polyol with HCFC 141b and water.

	Industry based polyurethane (PI)	Castor oil (HCFC 141b) (PCH)	Castor oil (Water) (PCW)
Chemical composition	1:1	1:1:0.25	1:1:0.015

For PI, non-blowing agent PU, polyol to isocyanate ratio is 1:1 signifies a balance between the use of polyol and isocyanate, with no additives required. The ratios were optimized to attain specific foam properties, including a balance of mechanical strength and lightweight characteristics with closed cells. The PCH ratio of polyol: isocyanate and HCFC-141b ratio was 1:1:0.25 indicates, attributed to the content of fatty acid chains in castor oil, which can affect the cell

structure and foam stability. A reduced amount of HCFC 141b is necessary to achieve the desired closed cell structure and adequate mechanical strength. The PCW ratio of polyol: isocyanate and water was 1:1:0.015. Water reacts with isocyanate, potentially consuming them in the process. An increased water ratio may diminish the effectiveness of isocyanates in urethane synthesis, thereby compromising the stability of the polymer network.

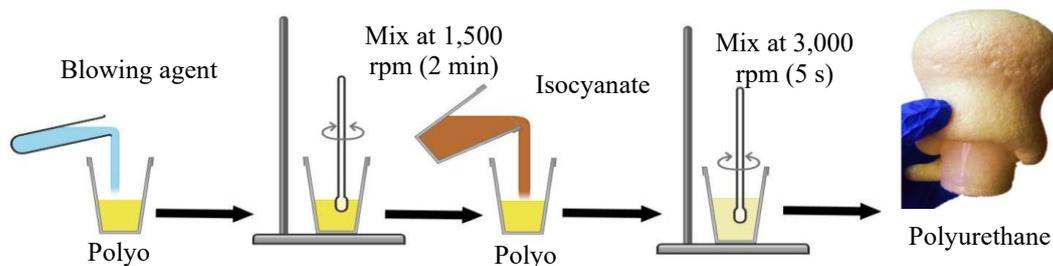


Figure 1 Schematic diagram steps in fabrication of polyurethane.

Measurements of properties of polyurethane

The polyurethane sample undergoes physical testing where measured its foam reaction time. The foam reaction time for the samples was determined by using ASTM D7487. The characteristics of the time that were shows on the **Figure 2**, were observed using

stopwatch during the foaming process in the plastic cup until it completely rises and loses its tackiness. **Table 3** shows the definition of each type characterization time that were measured. The synthesized were repeated 3 times to ensure consistency.



Figure 2 Steps to measure the characterization time.

Table 3 Definition of the characterization time.

Characterization of time	Definition
Cream time	Time taken for the reaction become white precipitated
Gel time	Time taken for the foam to become from liquid to gel
Rise time	Time taken for the foam sample to rise and stop
Tack free time	Time taken for the foam to become non sticky on the surface.

The apparent density was measured by including the outer skin of the polyurethane foam. After the sample were let 24 h for curing process takes places the samples were weighed and calculate its apparent density. Then, the steps were repeated for 3 times according to method ASTM D1622-08.

A rheology testing was to determine the ability of the polyurethane to expand and flow in a clear hose with opposite gravity of the earth’s direction. The hose was hold upright to ease the flow of the polyurethane resin. The sample was left to flow and expand until it hardened and stopped. The test was repeated 3 times to ensure the

distance travelled by the flow was calculated. The rheology testing was determined by using ASTM D4878 standard methods.

The Fourier Transform Infrared Spectroscopy (FTIR) analysis were analyzed by using FTIR spectroscopy by using ASTM E1252 methodology. The FTIR spectroscopy employed roughly 1 mg of each sample and its respective composition. The apparatus was set up to execute 16 scans at a resolution of 4 cm^{-1} . The acquired spectrum extended from $4,000$ to 500 cm^{-1} .

The samples were shaped into cubic forms, each with a side length of 5 cm, in preparation for compression testing. The compression testing of all types of polyurethane was conducted utilizing the Universal Testing Machine (UTM) in accordance with the ASTM D1621 standard, applying a load of 50 kN at a speed of 5 mm/min. The experimental methods were repeated 3 times for the data accuracy.

For morphology analysis, the sample were cut with dimension of a square of 50 mm on each side. The sample then will be coated in gold using the sputter coatings. Then, it was analyzed by using Scanning Electron Microscopy (SEM) with magnification of 80X with different angles of the sample. Then the image

analysis was performed using ImageJ software. The SEM images were calibrated using the provided scale bar. Cell size (diameter) was determined by measuring the Ferret diameter which the longest distance between any 2 points along the cell boundary of at least 50 - 100 individual cells randomly selected from each image. The cell size (area) and number of foam cell were calculated.

Results and discussion

Physical properties

Foam reaction time

Figure 3 shows the polyurethane industry (PI), castor oil- HCFC (PCH) and castor oil-water (PCW) after curing process takes place. The PCH sample have darker white colour compare to PCW. The distinguish in colour was because of the types of blowing agents used. As PCH was using HCFC-141b which is physical blowing agents, the HCFC is non-reactive with isocyanate, so the stabilizer interaction changed the colour due to residual of the catalyst. It also has undergone oxidation of aromatic isocyanates. As for PCW, the side reaction of reaction water to isocyanates may lead to more urea groups which was typically less coloured and may bleached the polymer matrix over time as the foam cures and oxidizes slowly.



Figure 3 Physical appearance of the polyurethane industry (PI), castor oil-HCFC (PCH) and castor oil-water (PCW).

The graph in **Figure 4** shows the time taken of the foaming process took place to produce PI, PCH and PCW. It is essential to record the cream time, the gel time, the rise time, and the tack-free time. to ensure the

consistency, quality, and optimal performance of the material in real-world applications [11].

The cream time for PI was 10.4 s, whereas PCH and PCW exhibited slightly longer cream times of 11.16

and 15.33 s, respectively. The increased presence of hydroxyl groups in polyurethane accelerates the foaming process, resulting in the shortest cream time for industrial polyurethane. The use of castor oil with water as a blowing agent accelerated the polyurethane foam reaction time compared to HCFC-141b, primarily because water interacts chemically with isocyanate, resulting in a rapid release of carbon dioxide (CO₂) and heat [12]. All types of polyurethane adhere to the standard for polyurethane grouting, which is 10 to 20 s.

Gel time implies the transition from a liquid state to a solid state. The gel time of castor oil based polyol polyurethane is significantly influenced by the types of blowing agents used [13]. The gel time for PCH is 7.36 s, which is longer than the gel times for PCW and PI, recorded at 6.43 and 2.35 s, respectively. **Figure 6** confirms that the reaction of water with isocyanate produces CO₂ and amines. This reaction increases the heat, thereby accelerating the crosslinking and gel time in the foam. The reaction between water and isocyanate competes with the isocyanate-polyol reaction, which may influence the gel time of the polyurethane system.

In contrast, HCFC-141b is chemically inert toward isocyanates and does not interfere with the polymerization process [14]. It expands via vaporization when subjected to heat from the exothermic polyurethane reaction. The delayed gas evolution facilitates a more consistent polyol and isocyanate reaction, resulting in extended gel times relative to water. A moderate gel time between 5 - 15 s is ideal for most grouting applications, as it allows sufficient flow while ensuring quick setting after placement [15].

Next, the compression testing of the polyurethane sample was determined by using ASTM D3574 methods. The sample size of 5×5×5 cm³ was compressed with load of 50kN. It was crucial to determine the compression strength and modulus of the polyurethane foam. The ASTM E 2089 scanning electron microscopy (SEM) method was performed at 40X magnifications. To evaluate polyurethane foam and distribution, the specimen's cross sectional dimensions were 10×10 mm. The shape of the cell form is an important aspect of defining the mechanical characteristics of polyurethane.

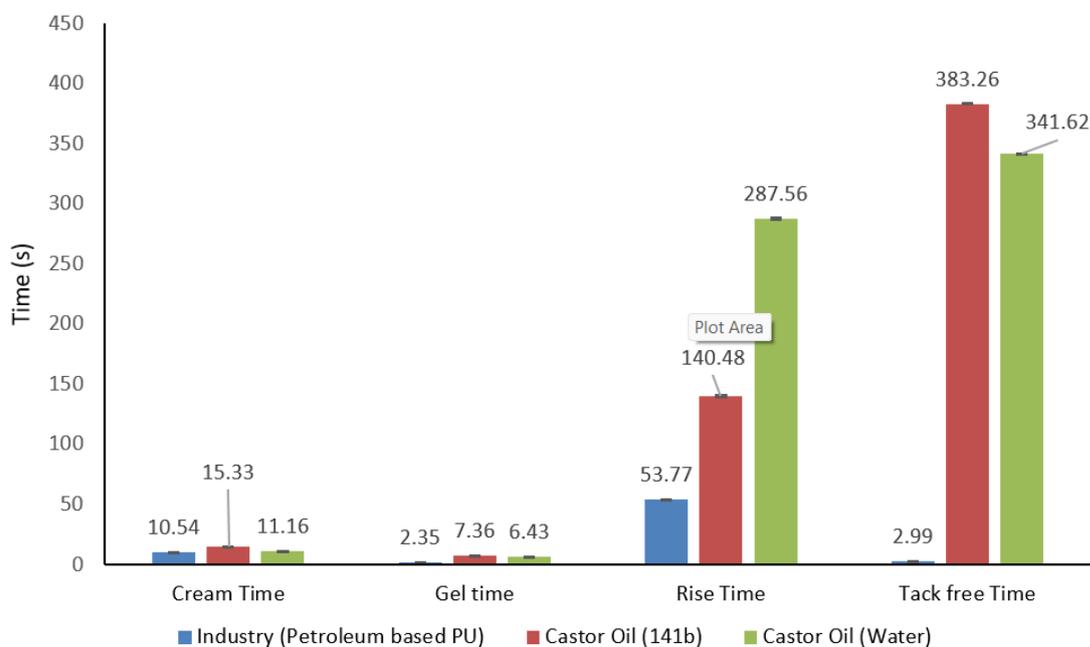


Figure 4 Foam reaction time of PI, PCH and PCW.

Rise time, defined as the duration required for polyurethane foam to attain its maximum size and final structure [16]. The rise time for PCW is significantly longer at 287.56 s, in contrast to PI at 53.77 s and PCH

at 140.48 s. Water interacts with isocyanates, resulting in the generation of carbon dioxide (CO₂), which facilitates foam expansion. The reaction between water and isocyanate competes to form the urethane

formation, thereby slowing the overall reaction kinetics and extending the rise time [9]. HCFC 141b chemically reacts with OH groups in polyol, resulting in physical expansion through vaporization caused by the heat generated during the reaction. This process occurs more rapidly than the chemical reaction of water, resulting in a reduced rise time [17]. Castor oil has different hydroxyl group configuration compared to polyurethane industry. The hydroxyl groups in castor oil are less reactive, which can slow the polymerization reaction and resulting in a longer rise time [18]. Castor oil is also a triglyceride-based, which may lead to lower crosslinking density and can slower reaction rates [19]. The addition of water as a blowing agent tends often has larger cells, reduced density, and potentially less uniform structure due to slower reaction kinetics of castor oil-based polyols. When combined the castor oil and HCFC-141b allows for a more gradual foam expansion, enabling better control over cell size and structure [20]. This can compensate for the naturally slower reaction rate of castor oil, resulting in higher foam density and more uniform cell morphology compared to water-based systems [19].

Finally, the tack-free time, which is the amount of time it takes for the foam surface to stop sticking [16].

Tack free time were longer for PCH and PCW as compared PI that only takes 2.99 s. PCW cured slower because the reaction between water and isocyanates produced carbon dioxide gas more gradually, resulting in a slower expansion and curing process. [12]. When water as blowing agent, it reacts with isocyanate and produced CO₂ gas and urea linkage as shown in **Figure 6**. The kinetics of the reaction can be influenced by the type of polyol used. Castor oil based polyol conditions may lead to slower gas generation due to lower reactivity in formation of polyurethane, contributing to a longer foam reaction time compare to industry based polyurethane [21].

Overall, PI reacts faster than the others. This is because PI tends to have a more regular, non-polar and less reactive structure which can be confirm as shown in FTIR spectra on **Figure 10** and SEM images in **Figure 13**, compared to PCH and PCW which have hydroxyl group attached to a more irregular, unsaturated fatty polymerization and foam formation. [17]. It shows that the 3 types of polyurethane not exceed the standard of polyurethane grouting for the foam reaction time which prove castor oil based polyurethane can be an ideal material to produce polyurethane to use as grouting materials.

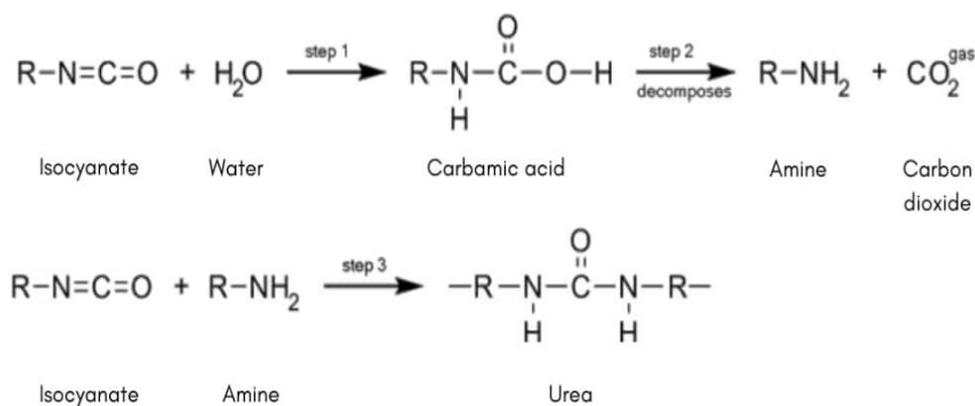


Figure 5 Chemical structure of water when react with isocyanate cited by Daniel Williams (2022).

combination of castor oil with a water blowing agent results in a material that is lighter, more flexible, and potentially superior in insulation properties due to its reduced thermal conductivity [22]. Lower density may reduce strength, however, castor oil based systems may still provide sufficient mechanical performance for certain grouting applications. The reduced density may be beneficial for effectively filling substantial voids or cracks while minimizing additional weight. This material is beneficial for filling gaps in building

insulation while minimizing additional weight on the structure. This enhances energy efficiency by reducing the rate of heat transfer through the structure [21].

PI has been used a lot previously because it works well to make dense foam. It is known, though, that it is bad for the climate and contributes to things like ozone depletion and global warming [17]. Water as blowing agent, is better for the environment because it poses fewer risks.

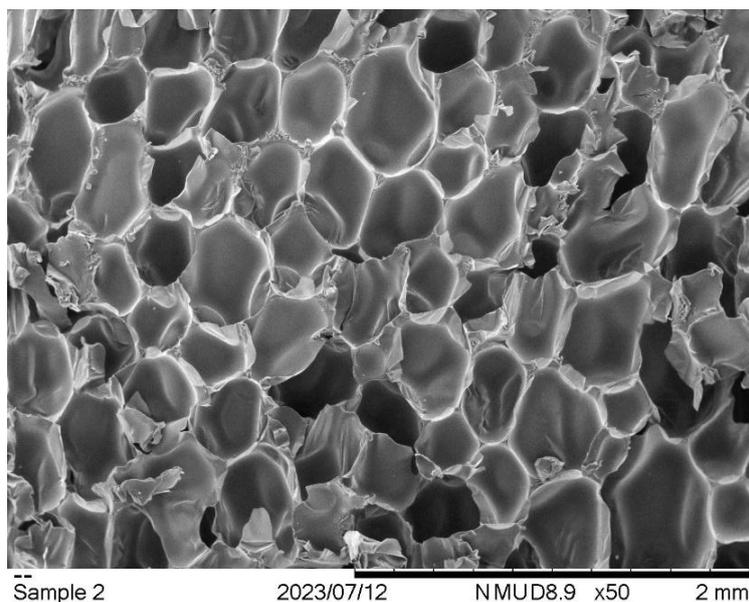


Figure 8 SEM images of rigid polyurethane with 50X magnification.

Rheology index

The rheology index quantifies the flow behavior of a material, typically linked to its viscosity. In the context of polyurethane foam, the index indicates the material's response to shear forces during the foaming process [19]. The rheology index was calculated by divided the distance of polyurethane travelled with the mass of polyurethane.

Figure 9 presents a rheology index of 2.25 g/cm for PI. This value indicates its balanced flow and process capabilities, typical of optimized formulations intended for industrial applications. However, it also suggests a material that exhibits slightly lower resistance to flow in comparison to PCH (2.4 g/cm) [19]. This indicates improved flow properties and superior mixing characteristics in the foam production process. HCFC-141b serves as an effective blowing agent, promoting enhanced gas generation and polymer expansion.

Higher values of the rheology index typically correspond to greater viscosity, indicating that the material is less able to flow [26]. Consequently, castor oil-based polyurethane exhibits slightly higher viscosity compared to conventional polyurethane used in the industry [21].

The higher rheology index of PCH indicates that it possesses the highest viscosity during processing. Increased viscosity may enhance resistance to flow, thereby aiding in the regulation of foam expansion and cell formation, resulting in a more uniform and stable structure [19]. The elevated viscosity may also lead to a marginally reduced expansion rate during the initial phases of the foam reaction, facilitating improved gas retention. **Figure 4** illustrates that the cream time of PCH is the longest in comparison to the other samples.

The lower rheology index of PCW results in a thicker, less fluid consistency, which is beneficial in

scenarios requiring controlled placement and reduced spreading. The PCW has less than 12.8% of the PI. The rheology index for 141b demonstrates superior flow characteristics for applications necessitating enhanced penetration and coverage relative to water [21].

A higher rheology index enhances standard polyurethane grouting by ensuring the material

effectively penetrates small areas and fills voids, resulting in more uniform and comprehensive coverage [23]. In structural repairs and soil stabilization projects, complete infiltration is essential to ensure the integrity and stability of the grouted area. All polyurethane foam exhibited rheological properties consistent with the range of industrial standard grouting materials.

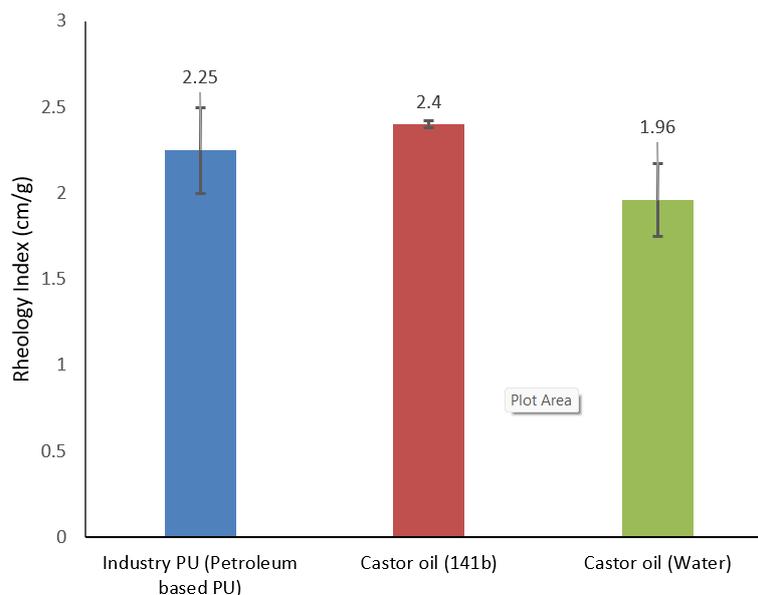


Figure 9 Rheology index of PI, PCH and PCW.

Fourier transform infrared spectroscopy (FTIR) analysis

Fourier Transform Infrared Spectroscopy (FTIR) is an analytical technique used to identify organic, polymeric, and in some cases, inorganic materials. Polyurethane is formed by the reaction between isocyanate and polyol. In the case of PCH and PCW, castor oil (a triglyceride with hydroxyl groups) is used as the polyol. HCFC-141b commonly used blowing agents in polyurethane foam production. However, water has emerged as a viable alternative. These agents help to create the cellular structure of the foam by generating gases during the polymerization process. [23].

Typically, PI is derived from industry-based polyols. The FTIR spectrum in **Figure 10** shown strong, well defined peaks corresponding to the urethane linkages, with little interference from other natural substances [24]. PCH and PCW have additional peaks related to the ester groups in the triglyceride structure of castor oil [24]. These appear around $1,730\text{ cm}^{-1}$ (C=O

stretching in esters). Castor oil hydroxyl groups ($-\text{OH}$) also contribute to the broad peak around $3,300 - 3,500\text{ cm}^{-1}$. HCFC-141b may introduce slight variations in the FTIR spectrum, particularly in the C–H stretching region ($2,800 - 3,000\text{ cm}^{-1}$) due to the presence of halogenated alkanes [25].

Water reacts chemically with isocyanates to form urea linkages ($-\text{NHCO}-\text{NH}-$), generating carbon dioxide gas that expands the foam. This reaction produces changes in the FTIR spectra. The presence of water as a blowing agent leads to new urea linkages, detectable through shifts or new peaks in the N–H and C=O regions. 141b, being chemically inert, does not contribute significantly to the FTIR spectrum but may introduce subtle changes in the aliphatic C–H stretching region [27]. It shows that the polyol chemical reaction is completed due to no excess of the isocyanate presence in the spectra.

The polyol component in PI is synthetic, resulting in cleaner spectra with fewer overlapping peaks. The spectrum typically shows well defined urethane and

urea absorption bands [25]. FTIR analysis of both PI, PCH ad PCW provides crucial information about the material’s chemical structure. The technique identifies the key functional groups involved, highlights the differences introduced by the type of polyol used, and

shows the effects of blowing agents, especially the water induced formation of urea linkages. These spectra used to confirm the success of the polymerization process and ensure the desired material properties have achieved.

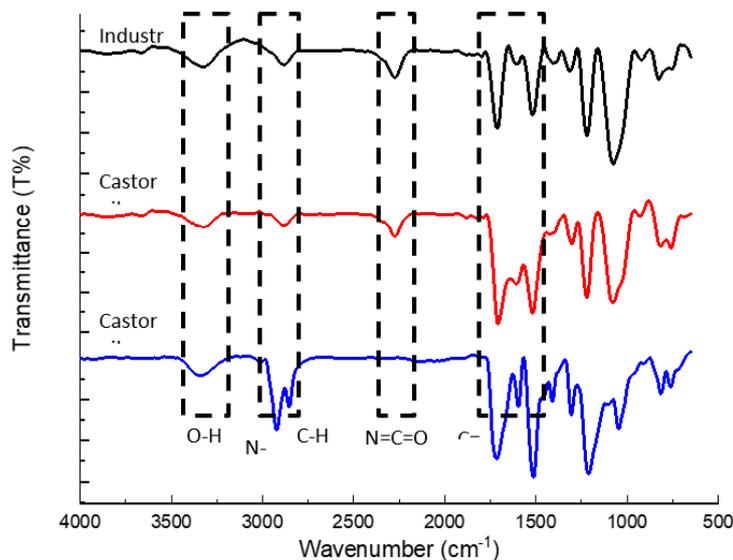


Figure 10 FTIR analysis of PI, PCH and PCW.

Table 3 FTIR spectra obtained for the 3 type of polyurethane (Industry, Castor oil HCFC-141b and Castor oil water) and possible functional group.

Reference (Wavenumber cm ⁻¹)	Industry (Wavenumber cm ⁻¹)	Castor oil HCFC-141b (Wavenumber cm ⁻¹)	Castor Oil Water (Wavenumber cm ⁻¹)	Functional Group (Wavenumber cm ⁻¹)
3,200 - 3,600	3,322	3,326	3,344	O-H
3,100 - 3,500	3,124	3,166	3,145	N-H
2,800 - 3,000	2,874	2,888	2,854	C-H
2,270 - 2,300	2,272	2,278	2,288	N=C=O
1,725	1,710	1,702	1,716	C=O

Mechanical properties

Compression strength analysis

Compression testing is a method used to measure how a material behaves when it is subjected to compressive (squeezing) forces. In this test, the material is compressed between 2 plates, and the force and deformation are recorded. This gives insights into several key properties, including the compressive strength. It is he maximum compressive load the

material can handle before failure (crushing or significant deformation) [27]. Compression set is important, as it describes the foam’s ability to return to its original shape after prolonged compression. The foam’s compressive strength will affect its suitability for applications like cushioning or insulation, where it might be subject to sustained or cyclic compressive forces [28].

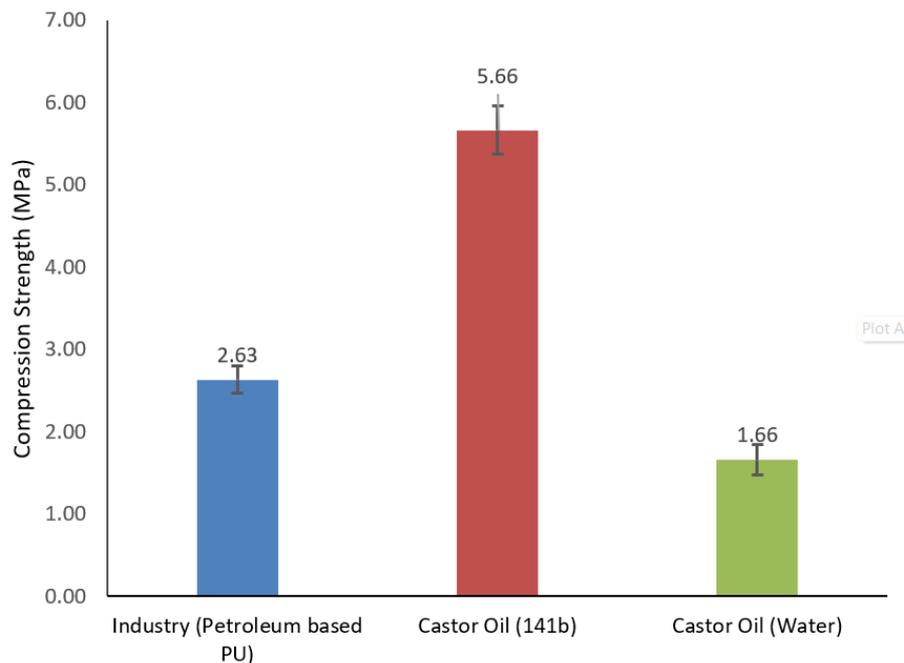


Figure 11 Compression strength of PI, PCH and PCW.

The **Figure 11** provides a comparative analysis of the compression strength of PI, PCH and PCW. The PCH polyurethane foam demonstrates a significantly higher compression strength of 5.62 MPa and in the range of industrial standard. This marked difference indicates that HCFC-141b promotes the formation of a denser, more uniform cellular matrix within the foam which illustrate as **Figure 13(b)**. The chemical characteristics of HCFC-141b likely led to more closed cells and fewer defects, enhancing the foam's mechanical robustness. The threefold increase in compression strength with 141b suggests that it is a superior blowing agent for applications requiring high strength polyurethane foams [29].

The density of polyurethane could influence the mechanical properties of polyurethane foam [30]. **Figure 7** showed that PI has a lower amount density than the PCH. Previous research indicates that the lower the density of the polyurethane, the less impact properties have in comparison to the higher density [31]. In addition, the size of the material's cells plays an important role in its mechanical properties. It is possible that larger sample cell sizes are weaker than smaller ones, but they may also be stronger [32]. **Figure 13(a)** demonstrates that the PI ratio is rigid polyurethane, which has closed-cell foam confirm by the SEM analysis. Even though the PI has lower value

compression strength (2.63 MPa) than PC, but its sufficient to prevent the cell from rupturing, as evidenced by the cell's inability to rupture as shown in **Figure 13(b)**.

The PCW demonstrates a compressive strength of 1.66 MPa, which is lowest compared to the PI and PCH, despite possessing a lower value and failing to meet the apparent density standard, as illustrated in **Figure 7**. This can be associated with the distinctive characteristics of castor oil, the role of water as a blowing agent, and the consequent foam construction. Castor oil possesses hydroxyl groups that augment the cross linking density throughout the process of polymerization. The addition of cross linking results in enhanced rigidity and compressive strength [30]. The triglyceride backbone and unsaturated fatty acids present in castor oil contribute inherent rigidity to the polymer matrix, resulting in enhanced mechanical properties even with a reduced density [23]. Despite the low density, the gas generated from the water isocyanate reaction has the capacity to create smaller, more uniformly distributed cells, as illustrated in **Figure 13(c)**. The interaction between water and isocyanates results in the formation of urea linkages, thereby enhancing the rigidity and strength of the polymer matrix. This addresses the low apparent density by offering enhanced compressive strength [31].

Compression modulus analysis

The **Figure 12** provides a comparative analysis of the compression modulus of polyurethane foam of PI, PCH and PCW. The compression modulus of polyurethane foams reflects their stiffness and deformation resistance, the compression modulus PI is 2.43 MPa, castor oil HCFC-141b is 7.78 MPa, and castor oil water is 2.16 MPa which highlight the differences in their stiffness corresponding to compressive forces. The compression modulus is directly influenced by the foam's apparent density, as it determines the distribution and connectivity of the solid phase in the cellular structure illustrate in **Figure 13** [32].

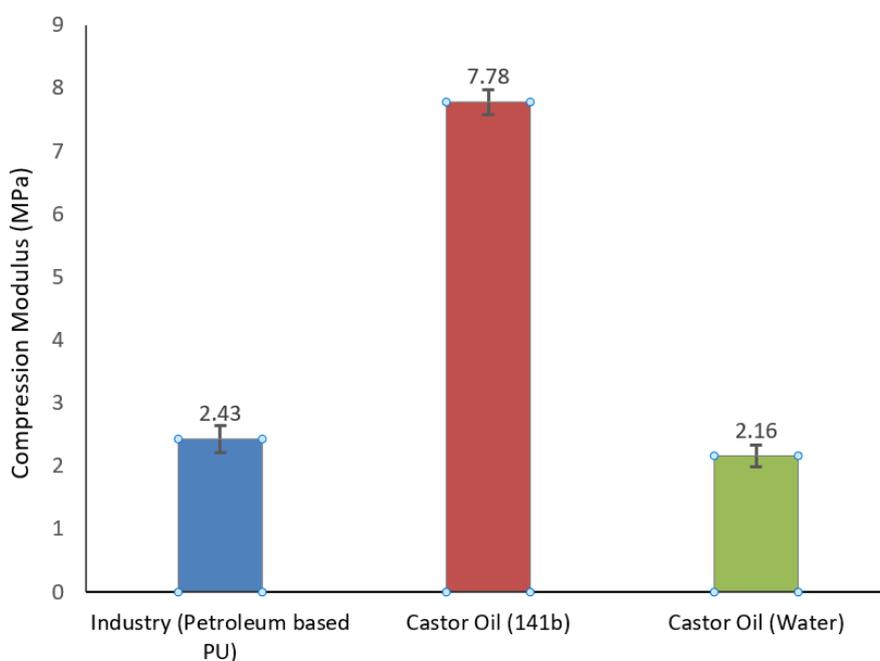


Figure 12 Compression modulus of PI, PCH and PCW.

The PCH exhibits a notably elevated compression modulus of 7.78 MPa. This suggests that the foam exhibits greater stiffness and enhanced resistance to compression. The increased modulus indicates that HCFC-141b facilitates the development of a denser and more uniform cellular structure characterized by smaller and more closed cells. This produces a foam that exhibits increased rigidity and can support greater loads with minimal deformation, as illustrated in **Figures 13(b)** and **13(e)** [29].

The PCW demonstrates a compression modulus of 2.16 MPa which is 11.1% less than PI. This value signifies that the foam exhibits relative flexibility and reduced

rigidity, attributable to the cellular structure developed when water serves as the blowing agent [28]. The interaction of castor oil and water results in a structure that balances stiffness and flexibility. This foam type is preferable for applications requiring a certain level of compressibility and cushioning [34].

As PI gives out the lower compression modulus it likely corresponds to the foam with a lower apparent density. But it has achieved the standard polyurethane grout for foam reaction time, apparent density and rheology index as shown the previous results graph. PI also not exhibits any cell rupture after doing compression as shown in **Figure 13(d)**. The choice of standard polyols and isocyanates in the industrial formulation provides sufficient toughness and flexibility to absorb compressive stresses without breaking. The foam formulation strikes a balance between elasticity, to recover after compression and rigidity to resist deformation. This balance allows the material to deform under load without cell rupture [33].

Morphological properties

The morphological properties of polyurethane, including the size and distribution of polymeric chains and crosslinking density, significantly affect their performance. Scanning electron microscopy (SEM) techniques reveal that industrial polyurethanes often

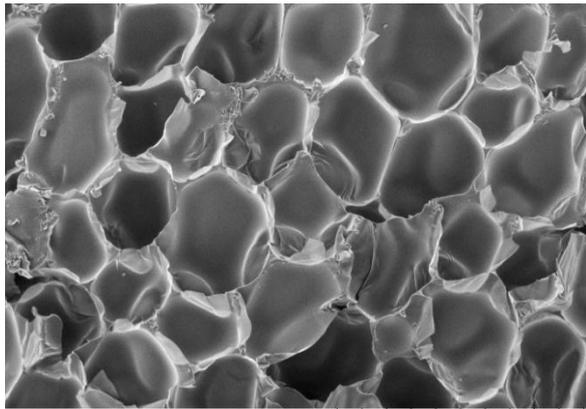
have a more homogeneous and consistent morphology, contributing to their high mechanical performance [34]. Green based polyol polyurethanes, while historically more heterogeneous due to variations in bio-based feedstock, have seen improvements in recent years. Through advanced processing techniques, green polyurethanes can now achieve a morphology that rivals or surpasses that of industrial polyurethanes, particularly in terms of crosslinking density and uniformity. The shape and size of the polyurethane foam cell are important to the mechanical properties [35].

Based on the SEM analysis portrayed in **Figure 13(d)** for the PI, the similar cell size and regular cell arrangement even after compress, demonstrate the excellent polyurethane mechanical and morphological properties. There is no broken cell wall presence in the cell arrangement. The same cell size and linear cell arrangement represent the rigidity of the sample which composed of more than 90% of closed cell [36]. The morphology PI foam, if the foam shows stable cell structure and is smaller in size (uniform cell), it will give good strength and modulus as shown in **Figures 11** and **12** [36]. Smaller cells size also helps to create a more uniform distribution of stress across the foam. It is shown in the cell area of PI in **Figure 14** which shows it has smallest cell size compare to castor oil polyurethane. This means that the stress is applied, it will not concentrate in one area, which can lead to early failure [37].

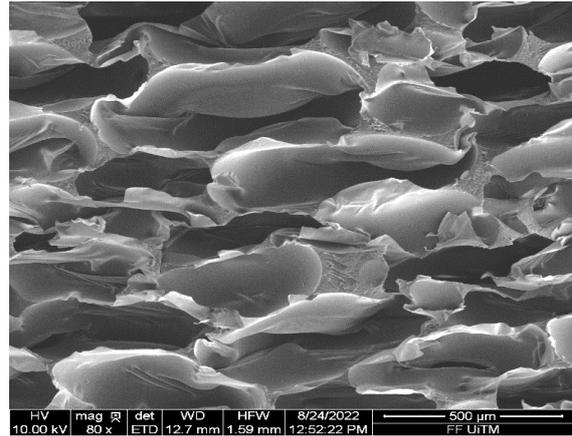
When a polyol and isocyanate react, the temperature of the mixture become increase because of

exothermic reaction. A physical blowing agent such as HCFC-141b vaporizes, utilizing the reaction heat. **Figure 13(b)** depict the PCH have irregular arrangement and cell size due vaporize of the HCFH-141b utilizing the reaction heat. It also shows by the graph of the cell distribution which indicate PCH have different cell size depicts in **Figure 15**. This is happening during rise time when bubble already formed, a new bubble nucleate that make a longer time to foam as shown in the **Figure 1**. [38]. But after conducted the compression testing, the cell wall did rupture but not enough changing the shape of the cell. This may due to the denser properties as shown in **Figure 7**.

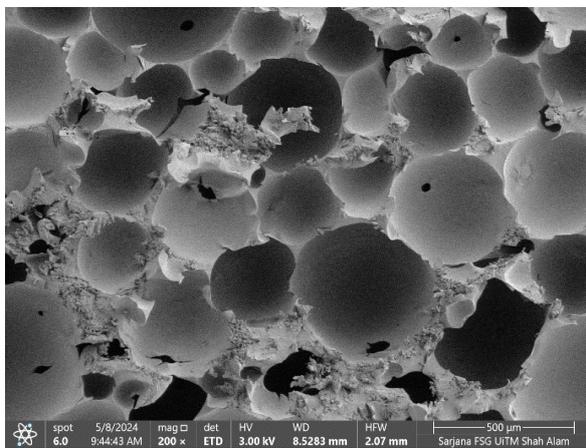
The images illustrate the microstructure of PCW, examined prior to and following compression. **Figures 13(c)** and **13(f)** illustrate the foam's initial microstructure. In this condition, the cells were well structured and consistently dispersed, exhibiting rather smooth walls despite having the lowest apparent density compared to the others, as well as lower values of compressive strength and modulus in comparison to PCH. **Figure 16** also confirm that the bigger size of cell of the foam can lead to lower in strength as shown in the **Figures 11** and **12** [37]. The interconnected cells indicate that the foam can efficiently absorb energy and collapse under pressure, rendering it especially appropriate for applications necessitating shock absorption, insulation, and cushioning, including packaging, beds, and soundproofing materials [22].



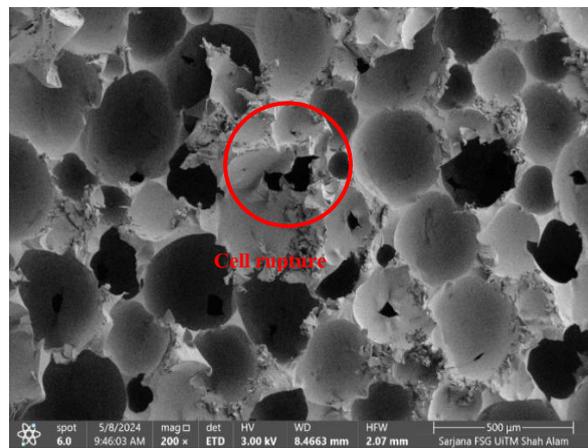
(a) PU industry (PI)



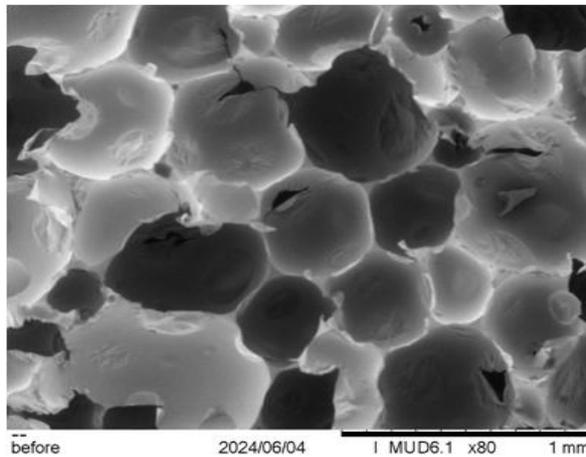
(d) PU industry (PI)



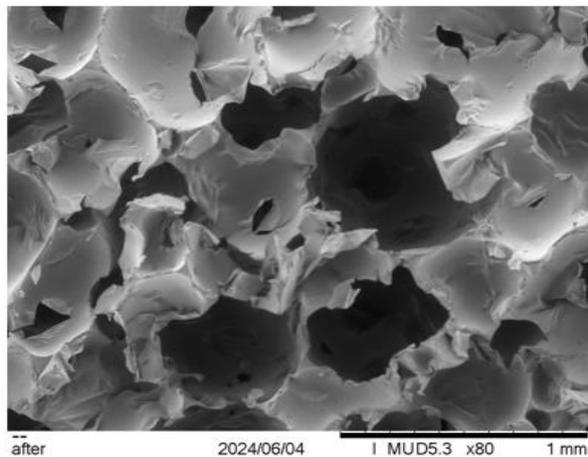
(b) Castor oil-HCFC 141b (PCH)



(e) Castor oil-HCFC 141b (PCH)



(c) Castor oil-water (PCW)



(f) Castor oil-water (PCW)

Figure 13 Morphology images of PI, PCH and PCW; (a), (b) and (c) before compression testing; (d), (e) and (f) after compression testing.

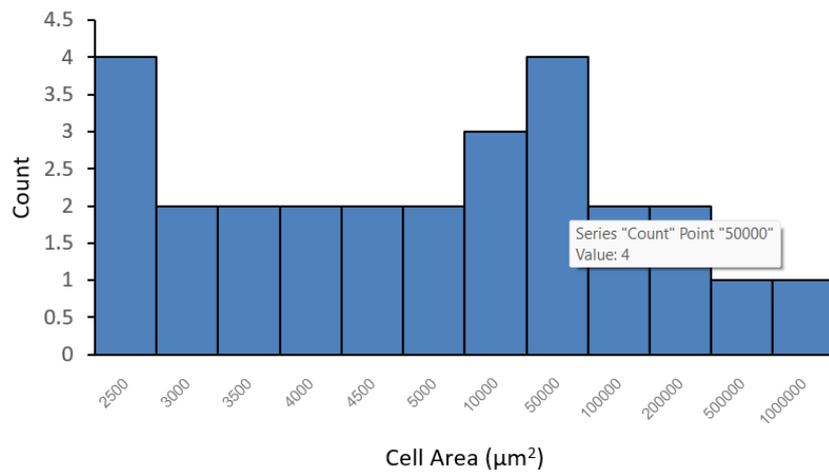


Figure 14 Cell distribution of the SEM images polyurethane industry (PI).

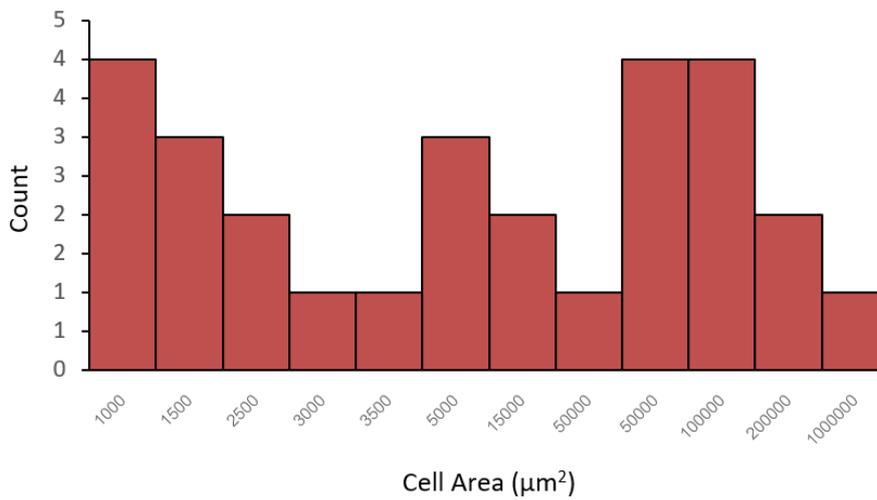


Figure 15 Cell distribution of SEM images castor oil-HCFC (PCH).

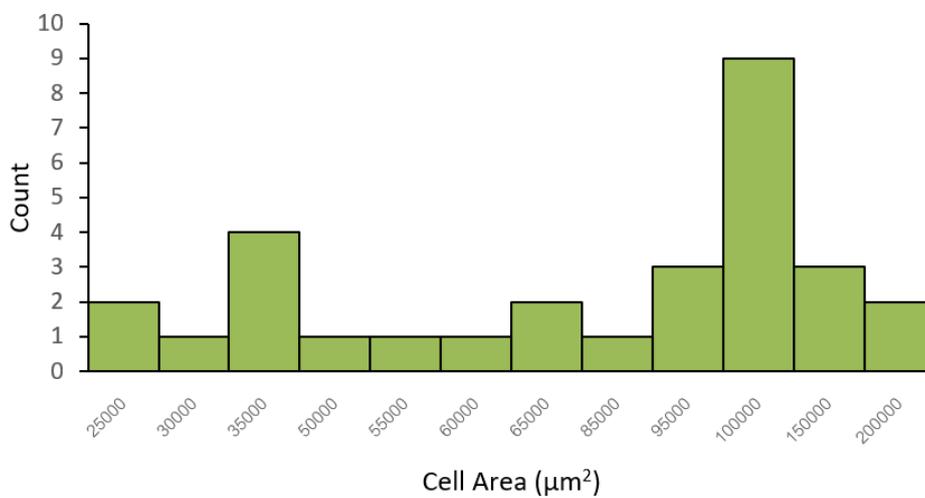


Figure 16 Cell distribution of SEM images castor oil-water (PCW).

Conclusions

Polyurethane was synthesized using industry-based polyol and isocyanate for standard applications, whereas green polyurethane was produced from castor oil, with HCFC-141b and water serving as blowing agents. This research indicates that both industrial and green polyurethanes fulfil the required performance criteria for grouting applications. While all 3 types of polyurethane meet grouting standards, castor oil water polyurethane presents a more environmentally sustainable alternative, maintaining mechanical strength and structural integrity. The apparent density is 45.66 kg/m³, with a compression strength of 1.66 MPa and a modulus of 2.16 MPa. This indicates a uniform structure of cell morphology and no evidence of gaps even after compression. The comparison of industrial and green polyurethanes reveals notable progress in the technology of green polyurethanes. Industrial polyurethanes (PI) currently dominate the grouting industry due to their established performance characteristics. However, castor oil based polyurethanes present a viable alternative, particularly as environmental concerns gain prominence. The findings indicate that transitioning to green polyurethanes in the grouting industry is both feasible and beneficial regarding performance and environmental impact. Although PCW does not dominate in performance, it still falls within the acceptable range for grouting applications. This represents a promising finding in the field of grouting, suggesting that with some adjustments to the water or castor oil ratio, the properties of PCW can be further enhanced properties of PCW. As for recommendation, a study related to field-stimulated such as Environmental Stress Cranking Resistance (ESCR) testing can be conducted as to study the degradation and the durability of the castor oil water (PCW) towards harsh environment. Also, a study on the Life Cycle Assessment (LCA) study comparing polyurethane industry (PI), castor oil-HCFC (PCH) and castor oil-water (PCW) in global warming potential (GWP) throughout their life cycle can be conducted. These future research can enhance industry collaboration, offer incentives for bio-based alternatives for a long term advantages of green polyurethane, as limited awareness, higher costs, and perceived poor performance hinder the adoption of green polyurethane in sectors dominated by traditional materials.

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Declaration of Generative AI in Scientific Writing

The authors acknowledge the use of the generative AI tools such as ChatGPT, Grammarly and QuillBot in the production of this manuscript, specifically on the editing and grammar correction. There are no content generation or data interpretation was performed by AI. The authors take liability for the data interpretation and conclusion of the manuscript.

CRedit Author Statement

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