



Comparative Studies on the Physico-Mechanical Properties of Polyurethane Foams Derived from Bio-Based Polyols

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Authors' contributions

This work was carried out in collaboration among all authors. All authors read and approved the final manuscript.

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ABSTRACT

The production of bio-based polyurethane foam (PUF) is a difficult process that necessitates substantial research. This paper describes the synthesis of PUFs from polyol derived from petroleum, castor oil, and shea butter fat. Polyurethane foams were produced in a single step using similar compositions of polyols, surfactant, catalyst, and isocyanate. The different polyol sources had an impact on the physico-mechanical properties of petroleum castor oil polyurethane foam (PPF), castor oil polyurethane foam (COPF), and Shea butter fat polyurethane foam (SBFPUF). In

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terms of isocyanate-water reaction and swelling time, SBPF outperforms COPF in cream and gel time. SBPF absorbed more water and had a larger apparent density than COPE. The high water absorption values in this study imply heavily cross-linked and complex foam formations with low impermeability. SBPF has greater tensile and compression strengths than COPF; however, COPF has better oil absorption and wear/abrasion resistance than SBPF. Castor oil-derived polyols had a greater impact on the oil absorption of polyurethane foams (PUFs) than SBF-polyols. Castor oil and SBF polyols, on the other hand, had comparable wear and abrasion effects. The increased compressive and tensile strengths of the foam demonstrate its load-bearing capability. The different sources of the polyols had a significant impact on the PUF alterations. Insulation, packaging, refrigeration, and other materials use castor oil and SBF polyurethane foams (PUFs). These foams' physico-mechanical properties make them appropriate for a variety of applications.

Keywords: Bio-based polyols; foams; physico-mechanical; polyurethane.

1. INTRODUCTION

Polyurethane (PU) is an exceptionally versatile polymer that offers a diverse array of practical uses, including foams, coatings, adhesives, and sealants, across several industries. Polyurethane foams (PUFs) are the most commonly used type of polyurethane (PU) in the industry, accounting for approximately 80% of PU applications. PUFs find extensive use in various fields, such as thermal insulation for construction and refrigerators, automotive seats, and cushions [1,2]. PUFs are commonly categorized as flexible, semirigid, or rigid foams based on their distinct physical and chemical characteristics. The diverse physical attributes of PUFs arise from the specific kind, and qualities of the raw materials, specifically polyols and isocyanates [3,4,5].

The characteristics of polyurethane (PU) are primarily influenced by the chemical composition and functionality of the polyol and isocyanate constituents, which are mostly controlled by the selection of monomers used in its production [4]. The utilization of multifunctional monomers with varied structures can result in the creation of branching, crosslinked, and dendritic structures, in contrast to the linear polymeric structures created by bifunctional monomers. The potential uses of these polymers can be determined based on their structure. For example, the advancement of linear polymeric fibre architectures that can be woven has the potential to achieve desirable mechanical properties [6,7,8]. Acquiring thermoplastic structures with less crosslinking is frequently advantageous as it enhances their ability to be processed and moulded [9,10]. On the other hand, polymers with a higher level of crosslinking may have enhanced heat resistance and mechanical characteristics, specifically in relation to modulus and compression [10].

Polyols, or polyhydric alcohols, are chemical compounds that consist of several hydroxyl (-OH) groups. These chemicals are commonly used as a monomer in various polymer products in industries such as food manufacturing, medicines, and the creation of polyurethane polymers and foams. Examples of polyols include glycerol, sorbitol, xylitol, erythritol, mannitol, polyethylene glycol (PEG), and malitol [11,12,13]. Petrochemical-derived polyols are costly and environmentally unfriendly. Additionally, they may lack the versatility, durability, and unique properties found in certain contemporary materials. For instance, they may not offer the flexibility required for upholstered furniture, beds, cushions, and vehicle seats, or the rigidity needed in buildings, appliances, and refrigeration systems [11]. Research has also documented the drawbacks of fossil-derived polyols on the coatings of materials, the potential of adhesives, sealants, and caulks, as well as their uses in the automotive industry, among others. Given the aforementioned factors, bio-based polyols have become a crucial requirement for several sectors.

Bio-based polyols are polyols derived from sustainable biological sources, such as plants or biomass. They function as a sustainable alternative to traditional polyols derived from fossil fuels, known as petrochemical-based polyols [7,14]. They are commonly used in the production of polyurethane goods, such as foams, coatings, adhesives, and sealants. Using bio-based polyols helps reduce dependence on finite fossil resources and has the potential to lower carbon emissions [15,16]. Feedstocks commonly employed in the manufacturing of bio-based polyols encompass Soybean Oil, Castor Oil, as well as diverse vegetable oils such as palm oil, canola oil, and sunflower oil [17]. The adoption of bio-based polyols aligns with the growing need for sustainable and eco-friendly

products [5,15]. It helps reduce the carbon emissions associated with the production of polyurethane products and fosters the development of a more sustainable and environmentally aware sector. However, it is essential to consider the entire life cycle of these materials, including their production, use, and disposal at the end of their existence, in order to assess their overall sustainability impact [11,18].

Polyols are considered the pliable constituent of polyurethane (PU) due to their alkyl chain, which allows for a certain degree of mobility. Using diols with a longer chain length in this context can lead to the formation of a polyurethane that is more flexible and stretchable. Using polyols with low molecular weight and high functionality can lead to a less flexible polyurethane (PU) material [18]. This occurs due to the reduction in the discrepancy between the number of segments that can bend or stretch and those that cannot, hence promoting the creation of connections between different parts. Thus, employing components possessing advanced functionality and robust chemical structures enables the production of inflexible polyurethane (PU) materials [19]. Moreover, specific polymers can be subjected to processing techniques that result in the formation of foams characterised by an enhanced surface area and a porous configuration, hence enabling a diverse array of potential applications. Large-surface PUF can be used for a wide range of high-end applications, such as water purification systems, biomedical scaffolds for cell regeneration, tissue engineering artificial skin, energy storage systems, effluent degradation, packing, insulation (both sound and thermal), cushioning, and build materials [20,21,22].

Polymers can be produced through the chemical reaction between a polyol molecule, which has several hydroxyl groups, and another component that has two or more isocyanate moieties. The polyaddition process involves the reaction between the nucleophilic oxygen group (-OH) and the electrophilic carbon (-N=C=O), leading to the formation of urethane bonds [22-25]. The isocyanate molecule (-N=C=O) is the fundamental component utilized in the synthesis of polyurethane (PU). The reactivity of isocyanates can be determined by the existence of a positive charge located at the carbon atom positioned between the nitrogen and oxygen atoms [22]. Isocyanate groups that are attached to electron-withdrawing groups, such as an aromatic ring, can amplify the positive charge

density on the carbon atom. This, in turn, leads to an increase in its reactivity. In contrast, electron-donating groups, such as an aliphatic chain, can decrease the reactivity of the isocyanate group [24].

Polyurethane foam materials require five essential reactants: (i) a polyisocyanate, (ii) polyol, (iii) catalyst system, (iv) surfactant and (v) blowing agent [10,18,24]. The influence of these reactants on the foaming process can be assessed by measuring foaming times, cream times, gel times, and tack-free times. Thus, the paper explores the comparative effect of the physic-mechanical properties of polyurethane foams obtained from petroleum polyol and bio-based polyols from Shea butter fats and castor oil for polyurethane forms.

2. MATERIALS AND METHODS

2.1 Materials

Petroleum polyol, castor polyol, shea butter polyol, toluene diisocyanate (TDI), Maxmech electric drill rated voltage (220-240V), mixing at 2500 to 3500 rpm, frequency: 50-60Hz, methylene chloride, dimethyl ethyl amine, stannous octate, water, silicone oil, wooden mould (102 cm x 51cm x 63cm), camry emperors weighing balance, S-mettlar balance (electronic).

2.2 Preparation of Foams

Polyurethane foams of petroleum polyol, castor oil and Shea butter polyols were manufacture by one step method, which was in line with Shin et al. [13]. In this method, the mixture of component of A (polyols, distilled water, catalysts, surfactant) and component B (toluene isocyanate) (see Table 1 for mass of the reagents) were stirred for 10 second with Maxmech electric drill rated voltage mixing at 2500 to 3500 rpm, with the frequency of 50-60HZ. The obtained mixture was immediately poured into a box. The resultant foams were allowed to cure at 80 °C for 15 min and they were removed from the box after 1 hour. During the synthesis of foams, catalysts responsible for reactions of isocyanate with water and polyols were used. Two competing reactions i.e. blowing and gelling may proceed in the absence of catalysts. Nevertheless, their rates are too low, therefore suitable catalysts had to be applied in order to conduct these reactions in a faster, controlled and balanced way. The catalyst formulation was selected experimentally in such a way that the gas produced was efficiently

Table 1. Formulations of polyurethane (PU) foam [13]

Components	Chemicals	Function	Mass (g)
A	Petroleum polyol, castor oil and Shea butter polyols	Polyols	100
	Silicone	Surfactant	2.5
	Dimethylethyl Amine (DMEA)	Catalyst (catalyst for TDI and water producing CO _{2(g)})	1
	Stannous Octate	Catalyst	1
	Methylene Dichloride	Blowing agent	3
	Water	Blowing agent b/w isocyanate and	7.5
B	Toluene diisocyanate	Isocyanate	55

entrapped in the polymer while foam cells had sufficient strength throughout the foaming process to maintain their structural integrity without collapse or shrinkage

2.3 Determination of Physical Properties

2.3.1 Density test

The foams' bulk density was determined using the Polish Norm PN-80/C-89035 (ISO 845). Three foam samples were extracted, each measuring 50 mm × 50 mm × 50 mm, and subsequently weighed with precision. The apparent density values were measured in kilogrammes per cubic metre (kg/m³) [14].

2.3.2 Water absorption test

A water absorption test was conducted on foam samples measuring 15x7x0.2cm³ in accordance with the ASTM D 570-98 e1 protocol. The water absorption was quantified by recording the initial and final weights of the foam sample after immersing it in distilled water in a measuring cylinder at room temperature for a duration of 24 hours. The surplus water present on the foam surface was entirely absorbed using tissue paper prior to reweighing [25]. The water absorption of foam was assessed using the given equation.

% Water absorption =

$$\frac{\text{weight of weight foam} - \text{weight of initial foam}}{\text{Weight of initial foam}}$$

2.4 Mechanical Properties

2.4.1 Compression strength test

The ASTM D 3574 - 11 test C, which is most suitable for flexible foams, was utilized in this study. The test specimen is cuboid in shape. The sample diameters are inputted into the display using the UNIVERSAL TESTER, which is a two column device. The sample is inserted between the platens of a compression-testing machine

with the slow application of a downward force/load, initiated by hitting the OK button. The machine operates at a speed of 50 mm/s. The machine ceased forward movement when it reached its maximum compression by compressing the flat surface until the foam was compressed by 1 inch (equivalent to 25 percent of the sample's 4 inch height) [21]. The machine recorded these data, after which the readings began to decrease. The mean compressive strength values were derived from three specimens per sample and expressed in kilopascals (kPa).

2.4.2 Tensile properties

The foam tensile strength test was conducted using the ASTM D3574 – 11, test E standard provided by the American Society for Testing and Materials (ASTM). The sample, which had a dumbbell-shaped (dogbone) structure, was sliced with the following dimensions: a length of 20 millimeters (mm) and a width of 10 ml. The resulting area was 200 mm² (20 x 10 = 200 mm²), and it was then inputted into the monitor. The machine's operational velocity was 50 millimetres per minute. The measurements were conducted at a crosshead speed of 100 mm/min. The tensile strengths were measured and expressed in kilopascals (kPa). The ultimate elongations were determined by subtracting the initial distances between the benchmarks from their overall distances at the moment of rupture.

2.4.3 Oil absorption

The absorption capacity of polyurethane foams was quantified using the ASTM F726-99 Standard Test Method for sorbent performance of adsorbents. The methodology for performing absorption tests on PU foam is described. Three beakers with a volume capacity of 500ml each were utilized. A quantity of 250 ml of oil or organic solvent sample was

poured into each of the three beakers individually. Prior to the immersion process, the initial dry weight of the PU sample (with dimensions of 1 cm x 1 cm x 1 cm) was recorded. Subsequently, the dehydrated polyurethane foams were placed into individual beakers and submerged for a duration of 5 minutes. After a duration of 5 minutes, the foam was extracted from the beaker using forceps and thereafter held for a period of 5 seconds to allow any surplus or weakly attached oil/organic solvent to drain. Subsequently, the saturated foam was promptly transferred to a high-precision digital scale with a reading of up to 0.001 g. The resulting weight, referred to as the saturated weight, was then documented. The absorption capacity of each PU foam sample was calculated using the equation;

$$\text{Oil Absorption} = \frac{S_t - S_o}{S_o}$$

S_o=Initial dry weight of the foam, and S_t= the weight of foam together with the weight of oil

2.4.4 Wear/abrasion resistance

The provided polyurethane sample was precisely cut and accurately weighed. The weight has been recorded and the machine is rotating at a speed of 200 revolutions per minute (rpm). The abrasion test is conducted using the ISO 4649/DIN 53516 standard. The specimen was

positioned onto the surface of an abrasive sheet that was affixed to a rotating drum. The weight/mass or volume loss technique was conducted for a duration of sixty seconds (60), and the results were measured and documented. Alternatively, it can be expressed as a proportion or ratio.

3. RESULTS AND DISCUSSION

3.1 Results

The results of this research work were presented in Table 1 and Table 2. The Table 1 contains physical characteristics of polyurethane foam derived from petroleum, castor oil, and Shea butter polyols. The parameters estimated include cream time, rise time, gel time, specific gravity, and water absorption. Table 2 contains the mechanical of polyurethane foam, like tensile strength, compression strength, oil absorption, and wear/Abrasion.

3.2 Discussion

3.2.1 Physical characteristics of polyurethane foam

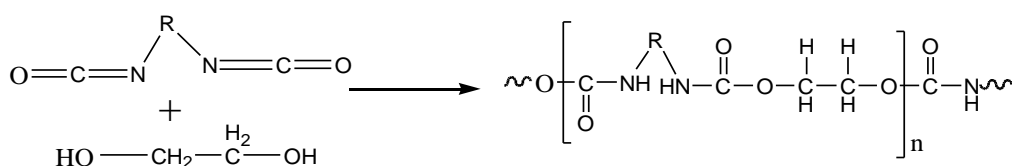
The reactions between isocyanate with water and polyols are highly exothermic. The carbon dioxide produced from the chemical interaction between the isocyanate and water serves as a foaming agent, causing the bubbles to grow. Concurrently, the primary structure of the urethane group is created through the gelation process involving isocyanate and polyols with from different sources like petroleum, castor oil, and Shea butter as depicted in Scheme 1.

Table 2. Physical Characteristics of polyurethane foam

Polyols	Petroleum Polyurethane Foam (PPF)	Castor oil Polyurethane Foam (COPF)	Shea butter Fat Polyurethane Foam (SBFPF)
Cream Time (s)	20	32	25
Rise Time (s)	600	1500	780
Gell Time (s)	13200	21485	17100
Specific gravity	0.035	0.038	0.039
Water absorption (%)	280	212	300
Apparent Density kg/m ³	34.6	50.4	55.2

Table 3. Mechanical of polyurethane foam

Polyols	Petroleum Polyurethane Foam (PPF)	Castor Oil Polyurethane Foam (COPF)	Shea butter Fat Polyurethane Foam (SBFPF)
Tensile strength (KPa)	75.0	65.0	70.0
Compression strength(KPa)	83.0	58.	65.
Oil Absorption	2.068	5.7	2.7
Wear/Abrasion	0.08	0.07	0.06



Scheme 1. Gelling reaction between the isocyanate and polyols

The cream time for castor oil polyurethane foam (COPF) was 32 seconds, while the cream time for Shea butter fat polyurethane foam (SBFPF) was recorded at 25 seconds (Table 1). The obtained values exceeded those of petroleum polyurethane foam (PPF), which were measured at 20 seconds under the same conditions. The gelation time of COPF was recorded at 21485 seconds, while the gelation time of SBFPF was 17100 seconds. Both COPF and SBFPF had gel times that exceeded those of PPF, which was measured at 13200 seconds. The gel time data suggests that the reaction between isocyanate and water in PPF was faster compared to SBFPF, and is subsequently followed by COPF. According to Vargas-Gutiérrez et al. [11] and Nsude et al. [19], the process of polymer network formation using polyols was rapid in PPF compared to SBFPF and COPF, as shown by the gel time. This aligns with the findings of Suleman et al. [25], who documented the gel time for the production of both flexible and rigid polyurethane foam. Lim et al. [27] conducted a study where they determined that the cream time and gel time of polyurethane foam derived from polypropylene glycols (PPGs) were around 90 seconds and 259 seconds, respectively. In a comparable work, Leng et al. [28] documented a cream time of 30 seconds and a low gel time of 28 seconds for polyurethane foams based on coconut fatty acid diethanolamide. In their study, Narine et al. [29] documented the cream time of Canola-PU, Soybean-PU, and Castor-PU as 10 seconds, 30 seconds, and 15 seconds, respectively. The gel time, on the other hand, was measured as 40 seconds, 90 seconds, and 50 seconds for the same samples. The SBF-polyol employed in SBFPF exhibits a shorter cream duration compared to the CO-polyol utilized in COPF.

The COPE of water absorption was 212%, the SBPF was 300%, and the PPF was calculated to be 280%. In a comparable study, Vargas-Gutiérrez et al. [11] documented a significant increase of 256% and 331% in the production of polyurethane foams derived from cassava starch and rice biomass, respectively. Kairyte et al. [14] observed a water absorption rate of 6.8% for bio-

based rigid polyurethane foam that was filled with ash residue from biomass incineration. Gursory and Alma [30] conducted a study on polyurethane foams made from potato waste. They found that these foams had a water absorption capacity ranging from 137% to 393% when exposed to varying concentrations of H_2SO_4 . According to Yusuf et al. [31], PUF made from modified castor oil polyols had a water absorption of 0.73–2.20%.

The measured apparent densities of PPF, COPF, and SBFPF were 34.6 kg/m^3 , 50.4 kg/m^3 , and 55.2 kg/m^3 , respectively. This finding aligns with the results reported by Kairyte et al. [14], who observed a value of 46.5 for modified PU foam. In their study on polyurethane foams derived from cassava starch and rice biomass, Vargas-Gutiérrez et al. [11] measured the densities to be 39E-3 g/cm^3 and 26E-3 g/cm^3 , respectively. Jasiūnas et al. [7] found that rigid polyurethane foams made with crude-glycerol derived biomass biopolyols had a high density of 78.91 kg/m^3 and 152.21 kg/m^3 . Li et al. [32] measured the density of polyurethane foams made from wheat straw with various isocyanates, and recorded a density of 107.5 kg/m^3 for both samples. In a comparable study, Yusuf et al. [31] ascertained the density of polyurethane foam (PUF) made from modified castor oil polyols within the range of 24.50–50.50 kg/m^3 . PUFs possessing strong water absorption, low swelling ratio, and appropriate density are advantageous for the utilization of flowery foam.

3.2.2 Mechanical properties of polyurethane Foam

The tensile strength of petroleum polyurethane foam (PPF), castor oil polyurethane foam (COPF), and Shea butter fat polyurethane foam (SBFPF) was measured to be 75.0 KPa, 65.0 KPa, and 70.0 KPa, respectively (Table 2). The data analysis of polyurethane foam indicated that PPF exhibited the maximum tensile strength, whereas COPF shown the lowest. Li et al. [32] documented the tensile strength of flexible polyurethane foams made from wheat straw with various isocyanates as 31.2 KPa and 41.4 KPa,

respectively. In their study, Zhang et al. [33] determined that the tensile strength of PUF made from *Juncus effusus* fibres for oil removal from water is 1.14 MPa, which is rather low. In their study, Dworakowska et al. [3] documented values of 120 KPa and 60 KPa for the modified and unmodified rapeseed polyurethane foam (PUF) samples, respectively.

The compressive properties of a cellular polymer are determined by intricate mechanisms arising from the existence of empty spaces and a network of solid plates or struts that create cell walls (cell membranes) and edges. The mechanical qualities of most polyurethane foams (PUFs) are primarily determined by their densities and the types of cells present, which can be either closed or open cells [4]. The compressive strength of petroleum polyurethane foam (PPF), castor oil polyurethane foam (COPF), and Shea butter fat polyurethane foam (SBFPF) was measured to be 83.0 KPa, 58.0 KPa, and 65.0 KPa, respectively. The bio-based polyurethane foams, specifically SBFPF, exhibit the maximum compressive strength compared to COPF. Additionally, the compressive potential of PPF surpasses that of the bio-based PU foam in the research. In a comparable work, Kairyte et al. [14] documented a significant compressive strength of 240 KPa. In their study, Jasiūnas et al. [7] determined that polyurethane foams created using various ratios of crude-glycerol derived from biopolyols had a significant compressive strength ranging from 34.0 to 114.25 KPa. In their study, Yusuf et al. [31] observed a significant compressive strength for polyurethane foam (PUF) made from modified castor oil polyols, ranging from 89.20 to 450.20 KN/m². Amran et al. [4] documented that stiff polyurethane foams derived from different isocyanate indexes of polyol obtained from liquefied oil palm biomass exhibited a notable compressive strength ranging from 100 to 130 KPa.

The oil absorption values for PPF, COPF, and SBFPF derived from various polyols were determined to be 2.07, 5.70, and 2.70, respectively. The data indicate that both PPF and SBFPF exhibit similar oil absorption values, while COPF demonstrates the maximum oil absorption. The elevated COPF value may be linked to the characteristics of the cellular pores [34]. Ng et al. [35] documented a substantial oil absorption rate of 42-50 g/g for polyurethane foam with a modified surface. Zhang et al. [36] calculated that PUF composites treated with

MnO₂ nanowires can absorb 4.54 g/g of edible oils. According to Hoang et al. [37], the oil absorption capacity of rice straw PUF was found to be 12.012 g oil per gramme of PUF. Duong and Burford [38] calculated a significant oil absorption rate of 67.8 grammes per gramme at elevated temperatures and with a high-density polyurethane foam (PUF).

Abrasion resistance describes the capacity of a material to endure wear and tear when subjected to friction. Increased friction accelerates the degradation of the component. The abrasion resistance of a substance is determined by its chemical composition. The wear and abrasion of PPF, COPF, and SBFPF derived from various polyols were measured to be 0.08, 0.07, and 0.06, respectively. All three PUFs examined exhibit identical abrasive behaviour. The high abrasive properties of thermoplastic polyurethane elastomers and the impact of molecular weight on the abrasive wear behaviours of thermoplastic polyurethane were reported by Xiao and Sue [39] and Ma et al. [40]

4. CONCLUSION

This study has examined the physical and mechanical characteristics of flexible polyurethane foams (PUFs) made from petroleum polyol, castor oil polyols, and Shea butter fat polyols. The foams were generated using identical formulations of polyols, surfactant, catalyst, and isocyanate. The cream time and gel time results indicate that the reaction between isocyanate and water, as well as the swelling time of SBFPF, outperforms that of COPF. The water absorption capacity and apparent density of SBPF exceeded those of COPE. The high water absorption values observed in this case are indicative of strongly cross-linked and complex foam structures, resulting in a low barrier to water permeability.

Regarding the mechanical properties of PUFs, SBPF exhibited superior tensile strength and compression strength compared to COPF. However, COPF has shown better oil absorption and wear/abrasion characteristics than SBPF. The polyols derived from castor oil had a greater impact on the oil absorption of polyurethane foams (PUFs) compared to the polyols derived from SBF-polyols. However, both castor oil and SBF polyols had an equivalent effect on the wear and abrasion properties. The increased

compressive strength and tensile strength demonstrate the foam's ability to bear loads. The observed alterations were highly associated with the chemical compositions of the utilized polyols. Polyurethane foams (PUFs) derived from castor oil and SBF-polyols have versatile applications in insulation, packaging, refrigeration, flotation, and other materials. These foams possess a wide range of physico-mechanical properties, making them highly suitable for many utilitarian purposes.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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