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Role of Bio-polyols in Enhancing the Mechanical and Thermal Properties of Sustainable Polyurethane Foams

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Abstract

This paper explores the role of bio-polyols in enhancing the mechanical and thermal performance of sustainable polyurethane foams (PURFs). Bio-polyols, derived from renewable feedstocks such as vegetable oils, lignocellulosic biomass, and glycerol, offer an environmentally responsible alternative to petrochemical polyols while enabling comparable material properties. The review examines how structural features of bio-polyols—including hydroxyl value, functionality, molar mass, aromatic content, and degree of unsaturation—affect crosslink density, compressive strength, elasticity, thermal stability, glass transition temperature, and flame retardancy of PURFs. Although certain bio-polyols, particularly those with long aliphatic chains, may reduce rigidity or thermal resistance, others such as lignin- and tannin-based polyols significantly enhance performance due to their inherent aromaticity. Key sustainability advantages include renewability, potential biodegradability, and alignment with circular economy goals, though challenges remain in cost, variability, and industrial scalability. Future opportunities lie in bio-isocyanate development, solvent-free processing, and improved modification strategies. Overall, bio-polyols represent a promising pathway toward high-performance, low-impact polyurethane foams, provided their chemical diversity is optimised for targeted applications.

Introduction

Polyurethanes form an integral part of the industrial complex, with applications in nearly every sphere, from packaging to insulation. The scale at which they are utilised is a testament to their excellent thermos-mechanical and physico-chemical features. Another factor contributing to their immense success is the number of building blocks available for use, which can be employed to produce several different types of polyurethanes, each customised to fit a particular application [1].

One of the main structures comprising polyurethanes is polyols. Polyols are compounds containing more than two hydroxyl groups. The conventional polyols majorly used in this industry are petrochemical in nature. They are incredibly harmful to the environment, and their extensive usage has already caused irreversible damage to our planet.

To confront this issue, the use of a more sustainable alternative, known as a bio-polyol, has been made. Bio-polyols are polyols derived from natural materials. Some examples include those derived from vegetable oils, such as soybean, castor, and palm oil polyols. Bio-polyols create polyurethanes with properties similar to those created with conventional polyols at half the environmental cost. Bio-polyols have a different effect on the properties of polyurethanes, often impacting the thermal and mechanical

properties. These alterations may prove to be hindrances in obtaining the desired properties, but can be overcome with the application of the correct bio-polyol in the correct amount.
Thus, the use of bio-polyols proves to be of paramount importance in lifting the strain off the already dwindling non-renewable resources by providing ecologically sound solutions, setting the course for a greener, more sustainable future.

Composition and Structure of Polyurethanes [11] [2] [3]
Polyurethane is a versatile polymer synthesised via a condensation reaction between an isocyanate and a compound containing two or more active hydroxyl groups, often a polyol.
The basic raw materials used for the manufacture of polyurethanes are polyols and isocyanates, and the individual properties of both directly influence those of the polyurethane. The characteristics of the hydroxyl group-containing polyols, such as their nature, functionality, and molecular weight, affect the degree of crosslinking and the flexibility of the polyurethane. The greater the number of reactive hydroxyl groups, the greater is the crosslinking and hence the rigidity.
The defining characteristic of isocyanates is the presence of reactive groups with the structure (-N=C=O). They are responsible for imparting strength to the polyurethane, facilitating cross-linking through their reactive functional groups.
During the course of the reaction, the isocyanate functional group reacts with the hydroxyl group of the polyol to form urethane linkages (-NH-CO-O-). The isocyanate to polyol ratio used affects the balance between rigidity and elasticity of the polyurethane, resulting in different materials depending upon the ratio. A greater quantity of isocyanate results in harder, more rigid materials, whereas higher polyol content makes them softer and more flexible.
Polyols and isocyanates, though they are the major components of polyurethanes, are not the sole factors affecting their properties. The properties of polyurethanes are also influenced by catalysts, chain-extenders, cross-linkers, surfactants and blowing agents, which have a significant impact on the polyurethane's morphology, density, and stability.

Bio-polyols: Sources and Characteristics [2] [3]
In recent years, there has been a rising demand for sustainable alternatives to conventional polyols, which are environmentally costly and non-renewable. This demand has driven the development of bio-polyols, materials with enhanced environmental benefits that serve the same purpose of forming polyurethane linkages by reacting with isocyanates, thereby producing polyurethane foams. Sources of bio-polyols include natural oils, glycerol, and lignocellulosic biomasses.
3.1. Natural oils—such as rapeseed oil, sunflower oil, and castor oil—are quite common in this field. Bio-polyols can be obtained from them through the modification of either the double bonds or the ester bonds. This functionalization can be carried out through several methods, including epoxidation followed by ring-opening, transesterification, hydroformylation, and ozonolysis. Bio-polyols derived from oilseeds are widely favoured as an alternative to conventional polyols because of their environmentally friendly nature. These oils are produced by pressing oilseeds, a raw material whose production has increased in recent years, making them a suitable and abundantly available substitute for the rapidly dwindling crude oils. However, using vegetable oils as bio-polyols competes with food and feed production.
3.2. Some plant oils are derived from second-generation bio-based feedstocks; thus, they do not compete with food production. One example of these oils is tall oil. Tall oil fatty acids, obtained through fractional

distillation of crude tall oil, have a high level of unsaturation. This unsaturation permits the introduction of hydroxyl groups via the breakdown of carbon-carbon double bonds.

3.3. Crude glycerol is a by-product of the natural oil and animal fat transesterification process. Refined crude glycerol has applications across several industries, including the polyurethane industry. However, its applications have been limited due to the expensive nature of the process.

3.4. Lignocellulosic biomasses consist of a composite matrix of cellulose, hemicellulose, and lignin. The properties of lignin, including its high availability, low cost, and the presence of aliphatic and phenolic -OH groups, make it highly suitable for creating high-value-added bio-based products such as bio-polyols. However, its structure still requires modification due to the presence of sterically hindered OH groups, which significantly reduce its reactivity. The liquefaction of lignins in the presence of polyhydric alcohols results in the formation of bio-polyols, which exhibit greater thermal stability because of the rigidity and aromatic character imparted to them. Although these serve as a suitable alternative to conventional polyols, they are produced through a process that involves high energy consumption at elevated temperatures. Therefore, the process is not sufficiently sustainable.

Thus, the composition and degree of chemical modification directly influence the hydroxyl functionality and polarity of bio-polyols, determining how they interact with isocyanates during polymerisation. This variability offers flexibility in designing polyurethane foams with tailored mechanical and thermal properties while advancing the goal of sustainability.

Effect of Bio-polyols on the Properties of Polyurethane Foams

The use of bio-polyols in polyurethane foams has several effects on their mechanical and thermal properties that impact their performance. This is due to the unique chemistry of the different types of bio-polyols discussed previously. Mechanical and thermal properties depend on the polymer network structure.

Chemical Features of Bio-Polyols That Influence Mechanical Properties

Hydroxyl value (OHv) is a measure of the amount of free hydroxyl groups present in a chemical substance. In the context of bio-polyols, higher OHv values tend to improve the compressive strength of the foams modified.

The mechanical properties of PURFs are directly influenced by their functionality. Increasing the concentration of a bio-polyol with a low functionality leads to inferior mechanical properties, such as a decrease in compressive strength and Young's Modulus on account of decreased cross-linking density. Higher cross-linking density leads to greater compressive strength, as observed in the case of foams based on tannin bio-polyols. The increased strength of these foams is also due to the presence of aromatic rings in tannin bio-polyols. Aromatic structures introduce rigidity into the polyurethane, thus increasing its strength.

Another important feature is molar mass: as the molar mass of the polyol decreases, the brittleness it imparts increases as a result of a decrease in the stability of linear dimensions.

Thus, the mechanical properties of polyurethanes are greatly influenced by the features of the bio-polyols comprising them.

Effects on Mechanical Properties

The compressive strength of PURFs is influenced by several factors. Most notably, they are the OHv values, the functionality, the degree of cross-linking, and the molar mass.

According to Prociak et al., it was observed that, for a polyurethane foam (PURF) formed using water as a chemical blowing agent, the bio-polyol of OHv=290 mg KOH/g was replaced with one having an OHv=670 mg KOH/g, and the compressive strength of the foam increased from 0.92 to 1.48 MPa [4].

The flexibility of the polyurethane matrix is increased by the usage of an oleochemical component containing long, linear chains of fatty acid residues, which have low cross-linking capability. This leads to a decrease in the degree of packing of macromolecules, thus resulting in increased flexibility. Because of this, the compressive strength of the PURF was greatly affected. Foams based on vegetable raw materials were thus characterised by lower compressive strength than those based on conventional polyols [5]. However, foams based on tannin bio-polyols have a greater compressive strength due to their aromatic nature, which imparts rigidity [4].

Foams based on vegetable oils tend to have greater elasticity and thus decreased brittleness. This is because of the presence of long aliphatic chains in the polyol, which lack the rigidity provided by aromatic structures. They also reduce the cross-link density because their structure results in relatively fewer reactive hydroxyl sites per unit length. This trend of increased elasticity is more pronounced in mustard oil polyols, according to a decrease in brittleness upon increasing the content of mustard oil reported by Borowicz et al [5].

An important property is the apparent density of the PURF. It has been observed that, on using plant-based polyols such as rapeseed oil, the apparent density of the PURF decreases due to a lower OHv of the bio-polyol. However, the higher viscosity of rapeseed oil polyols reduces the reactivity of the system, thereby increasing apparent density through the formation of foams with open-cell structures.

Hence, the mechanical properties of PURFs vary significantly with changes in bio-polyol structure and composition. They can both enhance and reduce the performance of a PURF, but with proper formulation and calculations, bio-polyols can easily meet, and even exceed, the standards set by petrochemical polyols.

Chemical Features of Bio-Polyols That Influence Thermal Properties

Polyurethane foams are primarily used as insulation material, so the study of the impact of bio-polyols on their thermal properties becomes increasingly important. Bio-polyols with aromatic rings present in them provide greater thermal stability on account of their rigidity, as is the case with lignin and tannin bio-polyols. The opposite effect is observed in the case of aliphatic chains, which decrease the rigidity and thus the thermal stability. The polyurethane also becomes more unstable to heat depending upon the degree of unsaturation in the bio-polyol, as one with a higher degree of unsaturation is more susceptible to oxidation upon exposure to heat. Thus, such a foam is more likely to undergo thermal breakdown. Another factor influencing thermal stability is crosslink density, which helps increase thermal stability because of a higher number of linkages between the polyols.

Effects on Thermal Properties

The thermal conductivity coefficient is the factor which determines the thermal insulation capabilities of the PURF. The lower the value of the coefficient, the greater the ability of the material to act as an insulator. The thermal conductivity is primarily influenced by the cell structure, apparent density, and the gas trapped inside the cells [6]. The PURFs modified with bio-polyols do not generally show much difference in comparison to those modified with petrochemical polyols with regard to thermal insulation. However, their insulation ability can be increased by modifying the structure of the polyurethane materials. For example, the use of polyols based on white mustard oil and DEG resulted in a slight increase in the thermal conductivity coefficient due to a decrease in the content of closed cells in the foam [5].

Thermal stability is largely dependent on the units comprising the bio-polyol, such as the presence of aromatic rings or the presence of unsaturation. It is also reliant on the rigidity of the polyol, as observed in PURFs modified with lignin bio-polyols, which impart great rigidity to the structure on account of the presence of aromatic rings in the complex [7]. The degradation temperature, the temperature at which a material begins to break down, may also be used as a measure of thermal stability. The degradation temperature is determined using thermogravimetric analysis (TGA). The onset of decomposition temperatures of polyurethane foams tends to increase with an increase in the natural content, thus it increases with the addition of bio-polyols [6].

Glass transition temperature, defined as the temperature at which a polymer transitions from a hard, glassy, rigid state to a soft, rubbery, flexible state, helps define the thermal properties of polyurethanes. The isocyanate used plays an important role in determining the glass transition temperature, as it generally possesses a higher one as compared to the polyol [8]. However, as is seen in the case of castor oil-based polyols, the glass transition temperature increases upon the addition of a polyol with a relatively higher functionality, irrespective of the isocyanate used.

Flame retardancy of PURFs is improved by the presence of aromatic rings in the bio-polyols. Due to the aromatic structure of tannin-based bio-polyols, the propagation rate of the flame decreased, thus showcasing improved flame retardancy [4]. Polyols derived from vegetable oils also improve this feature due to their unique chemical structure and the presence of hydroxyl groups [9].

Thus, thermal performance depends heavily on the chemical properties of the bio-polyols. There are some disadvantages offered, such as the decreased thermal stability of vegetable oil bio-polyols, but these can be overcome with the use of other, more suitable polyols with aromatic ring structures, which have many benefits when it comes to enhanced thermal properties. Therefore, with proper formulation, sustainable foams with ideal heat insulation properties can be developed.

Sustainability and Challenges

While polyurethanes have been around for decades, their impact on the environment was not realised for several years. By the time people noticed the consequences of their plundering nature, the ecological state of the planet had already been severely compromised. Today, scientists are working relentlessly in order to prevent further damage from taking place. Thus, the use of bio-polyols in polyurethane foams is significantly important.

The use of bio-polyols is becoming popular because they are capable of providing polyurethanes with properties comparable to those created using petrochemicals at a relatively negligible cost. A major benefit of using bio-polyols is their natural nature, which means that they can degrade environmentally, a direct reason for the reduction of polyurethane waste in our surroundings. Polyurethanes are also often recycled into polyols by the chemical method due to their thermal stability. Bio-polyols are also a renewable resource [10]; they are not limited by their availability like petrochemical polyols are. As their sources are a part of our natural environment, they can be continuously reproduced, with their extraction causing significantly less damage to the natural world. Thus, bio-polyols contribute meaningfully to circular economy principles by shifting polyurethane production toward renewable and regenerative resource streams.

However, there are some disadvantages posed as well, such as the adverse effects sometimes observed on the mechanical and thermal properties. For example, the use of bio-polyols with long-chain aliphatic structures, such as those derived from vegetable oils, significantly decreases the compressive strength and thermal stability of the foam created. Their production may also offer some challenges due to the higher cost of production as compared to petrochemical sources. Though there have been developments in processing techniques to limit this, many industries avoid large-scale adoption solely because of this factor.

Future Directions and Opportunities

The use of bio-polyols presents several clear benefits, but their disadvantages cannot be ignored. In order to overcome these disadvantages, several steps can be taken to ensure the safe, economic, and environmentally conscious production of polyurethane foams.

1. Modification with natural components: existing polyurethane foams can be modified using natural substances to increase their susceptibility to natural degradation. The polyurethane foams formed by using starch as a polyol have proven to be too brittle, but upon combining it with a synthetic polymer, a foam with different properties is created, which maintains the properties of the synthetic polymer while incorporating the hydrophilicity of starch, thereby making it easier to decompose. Thus, the introduction of appropriate groups into existing PURFs can help integrate sustainability with functionality [10].
2. Fully bio-based PU systems: in addition to bio-polyols, we can also employ the use of bioisocyanates in polyurethane systems [12]. Though challenges are still posed to this field, the use of bioisocyanates would be monumental to sustainability efforts, as it would effectively reduce greenhouse emissions and the dependence on petrochemical feedstock.
3. Solvent-free processing: solvent-free methods are being approached to eradicate the problem of evaporation, condensation, and purification of the solvent. Waterborne and non-isocyanate polyurethanes are some examples which are created without organic solvents. Waterborne polyurethanes are only gaining popularity on account of the restrictions on solvent-based coatings. The water-based adhesives are found to be non-toxic and non-poisonous to the environment. Though they have a longer drying time, their adhesion properties match those of solvent-based adhesives; thus, they are popularly used. The usage of solvents can also be diminished through their replacement with supercritical fluids, which have a negligible environmental impact [10].
4. Scaling sustainable synthesis routes: the most important advancement required in this field is the scaling of sustainable synthesis routes in order to fit sustainable models to industrial use. This would entail the need for coordinated advances across feedstock logistics, process engineering, economics, and regulatory frameworks.

Conclusions

This paper has examined the role of bio-polyols in advancing the sustainability of polyurethane foams, highlighting both their potential and the complexities surrounding their use. By synthesising existing literature, it becomes clear that bio-polyols offer more than a renewable alternative to petrochemical polyols—they introduce new chemical possibilities that can influence performance, processing, and environmental impact. Their adoption reflects a broader shift toward greener material systems, driven by concerns over resource depletion, carbon emissions, and the need for more circular production models.

At the same time, the discussion shows that the transition to bio-based polyurethane systems is not without challenges. Variability in feedstock composition, the need for consistent industrial quality, and concerns about long-term durability all indicate that bio-polyols cannot simply replace petrochemical polyols without thoughtful optimisation. Still, the emerging strategies for improved synthesis, modification, and large-scale implementation demonstrate that these hurdles are increasingly manageable.
Overall, the research suggests that bio-polyols represent a meaningful step toward more sustainable polymer technology. With continued innovation, standardisation, and industrial collaboration, they have the capacity to support high-performance polyurethane foams while significantly reducing environmental impact.

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