Development of bio-based polyurethane aqueous dispersions for industrial applications

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"Alice perguntou:
— Gato Cheshire, pode me dizer qual o caminho que devo tomar?
— Isso depende muito de para onde você quer ir - respondeu o Gato.
— Eu não sei para onde ir - disse Alice.
— Se você não sabe para onde ir, qualquer caminho serve."

Alice no País das Maravilhas
(Lewis Carroll)

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ABSTRACT

Polyurethanes (PU) are versatile polymers widely used in industrial sectors such as footwear, coatings, and adhesives. However, conventional PU production relies on fossil-based raw materials and organic solvents, raising environmental and health concerns due to the emission of volatile organic compounds (VOCs). In this context, aqueous polyurethane dispersions (PUDs) have emerged as a more sustainable alternative, using water as the primary dispersion medium while retaining the desirable mechanical and chemical properties of polyurethane systems. This dissertation aimed to develop and characterize bio-based aqueous polyurethane dispersions with more than 50% renewable content, targeting applications in the footwear industry. The formulations were prepared using bio-based DIEXTER polyols and synthetic biodegradable polyols (PCL 2000 and PCL 1000) for comparison, through a synthesis process designed to minimize solvent consumption. A total of nine dispersions were produced and characterized in terms of physicochemical, structural, and thermal properties, including pH, solids content, viscosity, particle size, zeta potential, water adsorption–desorption behaviour, film properties such as Differential Scanning Calorimetry (DSC), Thermogravimetric Analysis (TGA), water vapour permeability, Dynamic Mechanical Analysis (DMA) and adhesive performance through T-peel tests. The synthesized dispersions exhibited pH values near neutrality and solids content within the typical range for stable PUD systems. Biobased formulations exhibited colloidal stability comparable to the synthetic references, with zeta potential values of approximately −48 mV, indicating stable dispersions. The results also revealed differences in particle size and film properties depending on the polyol used. In permeability and adsorption/desorption tests, DTX155_2 exhibited a balanced behaviour comparable to the commercial reference, highlighting its potential for cork agglomerate applications, while DTX274_4 and DTX274_5 showed higher water vapour permeability, making them promising candidates for breathable coating applications. In terms of adhesive performance, the PCL-based systems exhibited higher peel strength, whereas the DTX-based dispersions showed lower adhesion due to the greater rigidity of the resulting films. Overall, the results demonstrate that bio-based polyols are a viable alternative for producing stable aqueous polyurethane dispersions with properties suitable for various applications in the footwear industry. This work contributes to the development of more environmentally friendly materials and highlights the potential of bio-based polyurethane systems within the framework of sustainable materials development.

Keywords: application for footwear industry, aqueous polyurethane dispersions, bio-based polyol, sustainability.

RESUMO

Os poliuretanos (PU) são polímeros versáteis amplamente utilizados em diversos setores industriais, como calçado, revestimentos e adesivos. No entanto, a produção convencional de PU depende de matérias-primas de origem fóssil e de solventes orgânicos, o que suscita preocupações ambientais e de saúde, dado a emissão de compostos orgânicos voláteis (VOCs). Nesse contexto, as dispersões aquosas de poliuretano (PUDs) surgem como uma alternativa mais sustentável, uma vez que utilizam água como principal meio de dispersão, mantendo as propriedades mecânicas e químicas desejáveis dos sistemas de poliuretano. Esta dissertação teve como objetivo desenvolver e caracterizar dispersões aquosas de poliuretano de base biológica com mais de 50% de conteúdo renovável, visando aplicações na indústria do calçado. As formulações foram preparadas utilizando polióis biobased DIEXTER e polióis sintéticos biodegradáveis (PCL 2000 e PCL 1000) para comparação, por meio de um processo de síntese projetado para minimizar o consumo de solventes. Um total de nove dispersões foi produzido e caracterizado quanto às suas propriedades físico-químicas, estruturais e térmicas, incluindo pH, teor de sólidos, viscosidade, tamanho de partícula, potencial zeta, comportamento de adsorção–dessorção de água e propriedades dos filmes, tais como Calorimetria Exploratória Diferencial (DSC), Análise Termogravimétrica (TGA), permeabilidade ao vapor de água, Análise Dinâmico-Mecânica (DMA), além da avaliação do desempenho adesivo por meio de ensaios T-peel. As dispersões sintetizadas apresentaram valores de pH próximos da neutralidade e teor de sólidos dentro da faixa típica para sistemas PUD estáveis. As formulações biobased apresentaram estabilidade coloidal comparável à das referências sintéticas, com valores de potencial zeta em torno de −48 mV, indicando dispersões estáveis. Os resultados também revelaram diferenças no tamanho de partícula e nas propriedades dos filmes dependendo do poliol utilizado. Nos ensaios de permeabilidade e adsorção/dessorção, a amostra DTX155_2 apresentou comportamento equilibrado comparável à referência comercial, destacando seu potencial para aplicações em aglomerados de cortiça, enquanto as amostras DTX274_4 e DTX274_5 apresentaram maior permeabilidade ao vapor de água, tornando-se candidatas promissoras para aplicações em revestimentos respiráveis. Em termos de desempenho adesivo, os sistemas baseados em PCL apresentaram maior resistência ao descolamento, enquanto as dispersões baseadas em DTX apresentaram menores valores de adesão devido à maior rigidez dos filmes obtidos. De modo geral, os resultados demonstram que polióis de origem biológica representam uma alternativa viável para a produção de

dispersões aquosas de poliuretano estáveis, com propriedades adequadas para diversas aplicações na indústria do calçado. Este trabalho contribui para o desenvolvimento de materiais mais ambientalmente sustentáveis e destaca o potencial dos sistemas de poliuretano biobased no contexto desse desenvolvimento.

Palavras-chave: dispersões aquosas de poliuretano, indústria do calçado, poliol de base biológica, sustentabilidade.

SUMMARY

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ACRONYMS AND ABBREVIATIONS

ANOVA	Analysis of variance
CAGR	Compound annual growth rate
DBTDL	Dibutyltin dilaurate
DMA	Dynamic Mechanical Analysis
DMPA	Dimethylol propionic acid
DSC	Differential Scanning Calorimetry
E'	Storage modulus (mPa)
E"	Loss modulus (mPa)
EDA	1,2-ethylene diamine
IPDI	Isophorone diisocyanate
PU	Polyurethanes
PUD	Polyurethane dispersions
Tan δ	Samping factor
TEA	Triethylamine
T_g	Glass transition temperature (°C)
TGA	Thermogravimetric analysis
T_m	Melting temperature (°C)
VOCs	Volatile organic compounds
WBPUU	Waterborne polyurethane-urea dispersions
Wa	Water absorption (mg/cm²)
Wd	Water desorption (%)
WVP	Water vapour permeability (g/h.mm.Pa)
WVTR	Water vapour transmission rate (g/h.m²)

1 MOTIVATION AND OBJECTIVES

With technological advances and growing environmental concerns, the industry has been seeking more sustainable alternatives, particularly in the polymer sector. Among the various materials, polyurethanes (PU) stand out for their mechanical properties, flexibility, and chemical resistance. These properties make them highly versatile and widely used in industries such as footwear, where they play a crucial role in creating adhesives for product assembly [1].

Although conventional PUs offers high performance, their manufacture relies on fossil resources and organic solvents, which pose environmental and health risks due to the release of volatile organic compounds (VOCs) [2]. In this context, aqueous polyurethane dispersions (PUDs) emerge as more sustainable alternatives, using water as a dispersion medium without compromising essential functional properties [3].

PUDs were usually manufactured in four main stages: (i) prepolymer synthesis, which consisted of the reaction between polyols and diisocyanates; (ii) neutralization, in which ionic groups were incorporated to ensure stability in an aqueous medium; (iii) dispersion in water, a key step that replaced the organic medium with the aqueous phase, reducing or eliminating the use of organic solvents; and (iv) chain extension, which modified the molecular weight and defined the final properties of the polymer [4]. The flexibility of this process allowed the creation of formulations that could be adjusted to the demands of various industrial applications.

In the footwear industry, PUDs stood out as eco-friendly adhesives that provided mechanical strength, flexibility, and durability while significantly reducing VOC emissions. In addition, they could be used as coatings and as agglomerates in cork composites. This met growing regulatory, social, and environmental demands, and was especially important for adhesion between substrates such as leather, fabrics, and polymeric materials [5].

The main objective of this work was to develop and characterize aqueous polyurethane dispersions with more than 50% biobased content. These PUDs were formulated with bio-based polyols and were intended for various uses in the footwear industry, particularly for application as adhesives, coatings, and cork agglomerates. These PUDs were formulated with bio-based polyols and were intended for various uses in the footwear industry, such as adhesives, coatings, and cork agglomerates. Several PUD formulations were developed and analysed for their physicochemical, structural, and thermal characteristics (pH, solids content, viscosity, particle size, zeta potential, electrolytic stability, DSC, TGA, DMA, water vapour permeability, water adsorption, and desorption capacity), as well as their adhesive strength on

representative substrates. The results were compared to those made from synthetic raw materials to evaluate the feasibility of using biobased systems as a more sustainable option that met the footwear industry's technical and environmental requirements.

1.1 Structure of the work

This dissertation is organized into seven chapters, presenting the development of the research from its motivation and theoretical background to the main conclusions and supporting information.

Chapter 1 introduces the motivation and objectives of the study, highlighting the need for more sustainable materials and the relevance of aqueous polyurethane dispersions (PUDs), particularly those based on bio-based polyols.

Chapter 2 presents the bibliographic review, covering the fundamental concepts related to polyurethanes, aqueous polyurethane dispersions, their synthesis methods, properties, and applications, with emphasis on sustainable and bio-based systems.

Chapter 3 describes the methodological procedures adopted in this work, including the materials used, the synthesis of aqueous polyurethane dispersions, and the preparation of films and cork-based composites, as well as the characterization techniques employed.

Chapter 4 presents and discusses the results obtained, analysing the influence of formulation parameters on the physicochemical, structural, thermal, and mechanical properties of the developed dispersions, as well as their performance in potential applications.

Chapter 5 summarizes the main conclusions of the study, highlighting the most relevant findings and their contribution to the development of more sustainable polyurethane systems.

Finally, Chapter 6 compiles all the references cited throughout the dissertation.

2 BIBLIOGRAPHIC REVIEW

2.1 Advancement of Polymeric Materials

Polymeric materials have played a transformative role in industrial and technological development and continue to be fundamental in a variety of sectors, such as automotive, civil construction, packaging, textiles, medical, agricultural, and footwear. This wide range of applications stems from their versatility, low cost, lightness, and ease of processing, characteristics directly related to the diverse chemical structures and physical-mechanical properties of these materials. [1].

Initially derived from natural sources such as rubber, starch, cellulose, and proteins, synthetic polymers became widely used thanks to key discoveries like vulcanization in the 19th century and Hermann Staudinger's recognition of polymers as macromolecules in the 1920s [1,6]. The 20th century saw the consolidation of the synthetic polymer industry, with the emergence of materials such as polyethylene, polypropylene, PVC, polystyrene, polyamides, polyesters, and polyurethanes. These materials replaced traditional materials such as metals and glass due to their sustainability, chemical resistance, and lightweight nature [1].

However, in recent decades, the large-scale production and disposal of synthetic polymers, mostly derived from fossil sources, has become a cause of urgent environmental concern. In 2023, global plastic production reached approximately 400 million tons per year, more than double the 234 million tons produced in 2000 [7].

It is estimated that since 1950, more than 9 billion tons of plastic have been produced, with more than half of that total manufactured after 2004. This exponential increase in production has resulted in considerable environmental challenges, including the accumulation of plastic waste, greenhouse gas emissions, and the intensive consumption of non-renewable resources. Only about 9% of plastic waste is recycled globally, while the rest is incinerated, disposed of in landfills, or pollutes the environment [7].

Given this scenario, the industry has been seeking more sustainable alternatives to synthetic polymers, focusing on developing bio-based, biodegradable, and recyclable polymers that reduce environmental impact without compromising technical performance. This search is in line with projections for global bioplastics production capacity, which is expected to grow significantly from around 2.18 million tons in 2023 to approximately 7.43 million tons in 2028 [8].

For the development of new materials, it is essential to understand their origins, classification, and applications, particularly given the growing demand for sustainable

solutions. Thermal behaviour is an important criterion, as it allows materials to be classified into two main groups: thermoplastics and thermosets. In this scenario, polyurethane (PU) stands out as a unique polymer due to its versatility, as it can be synthesized in thermoset and thermoplastic forms, depending on the raw materials and synthesis conditions used. This duality, together with the possibility of renewable-based formulations, establishes PU as one of the most significant materials from technological and environmental perspectives today [6].

2.2 Polymer characteristics

Polymers can be classified according to their chemical, physical, and behavioural characteristics in the environment. An essential classification that has a major impact on the recyclability of materials is the distinction between thermoplastics and thermosets. This distinction not only reflects structural differences, but also directly affects their physical behaviour [9].

Thermoplastic materials require heat to become mouldable, forming a viscous liquid, and, after cooling, they retain the shape they acquired during moulding. These materials can be reheated and moulded repeatedly into new shapes without significant changes in their mechanical properties [10].

On the other hand, thermosetting plastics are polymers designed to maintain permanent shapes, undergoing chemical reactions that make them impossible to remelt or remold. These materials do not convert into a viscous liquid when exposed to high temperatures, as they degrade or decompose [10].

According to Callister (2020), thermoset polymers become rigid due to covalent cross-links that prevent softening upon heating and render remoulding or reprocessing impossible. These cross-links also provide greater resistance to high temperatures than thermoplastics do because only excessive heating can break them, leading to polymer degradation. Consequently, thermosets are generally harder, more resistant, and exhibit better dimensional stability. Examples include vulcanized rubbers, epoxies, phenolic resins, and certain polyester resins [9].

Table 1 shows some of the differences and applications of thermoplastics and thermosets. It should be noted that while thermoplastics are easier to recycle, thermosets offer greater thermal resistance and dimensional stability.

Table 1 – Comparison between thermoplastic and thermoset polymers in terms of structure, properties, processing, and typical applications [9,11]

Characteristic	Thermoplastics	Thermosets
Molecular structure	Linear, with weak bonds between chains	Networked, with strong bonds between chains
Melting temperature	Lower than the degradation temperature	Higher than the degradation temperature
Mechanical	Flexible and elastic; Good impact resistance	Rigid and brittle; Low impact resistance
Recyclability	Recyclable through the use of heat and pressure	Not recyclable
Operating temperature	Low continuous use temperature	High continuous use temperature
Material	Polyethylene, polystyrene, PVC, thermoplastic polyurethane (TPU)	Vulcanized rubbers, epoxy, phenolic resins, polyester, thermoset PU
Applications	Toys, household appliances, footwear, automotive, flexible adhesives (TPU)	Automotive, electrical, construction, rigid foams, structural adhesives

A particular case of this classification is PU, a polymer widely used in industrial applications, from rigid and flexible foams to coatings, adhesives, and elastomers [12]. This polymer can have thermoplastic or thermoset characteristics, depending on its formulation for the desired application.

This characteristic allows PU to meet different performance requirements, but also directly influences its recyclability. While thermoplastic versions can be melted down and reused through mechanical processes, thermoset versions, commonly found in foams and structural adhesives, are more complex to reuse, requiring techniques such as chemical recycling or energy recovery [13].

Thus, PU stands out not only for its wide applicability but also for the challenges it poses regarding reuse and environmental impact. The duality between its thermoplastic and thermosetting forms further complicates its management throughout its life cycle.

2.3 Polyurethane's chemistry

Polyurethanes are polymers formed by reacting polyols with isocyanates, usually in the presence of additives, catalysts, and chain extenders, depending on the intended application. This reaction is a type of polycondensation, in which hydroxyl (-OH) groups of polyols react with isocyanate (-N=C=O) groups, forming urethane (-NH-CO-O-) [14], as shown in Figure 1.

The ratio of reactants, the chemical structure of the polyols (linear or branched), and the type of isocyanate used (aromatic or aliphatic) directly influence the material's final

properties, such as stiffness, flexibility, thermal resistance, and chemical stability [4,14]. The most common diisocyanates are TDI (toluene diisocyanate) and MDI (diphenylmethane diisocyanate), while polyols can be, e.g., polyether or polyester in nature, with different molar weights and functionalities [15].

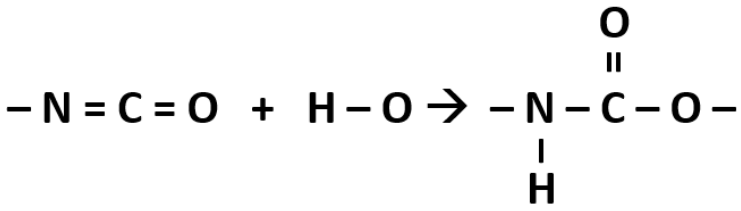

Figure 1 – Reaction between isocyanate and hydroxyl groups leading to the formation of the urethane linkage.

The molecular weight of the polyol is one of the main factors determining the final properties of PU [16]. Low-molecular-weight polyols (less than 1000 g/mol) generally form shorter chains, which confer PU properties such as high rigidity, a densely cross-linked structure, hardness, and thermal resistance. These attributes are desirable for hard coatings, rigid foams, and applications that require greater robustness. On the other hand, high-molecular-weight polyols (greater than 2000 g/mol) produce longer, more flexible chains, which facilitate the manufacture of malleable, elastic polyurethanes with lower density, such as elastomers, flexible foams, and polyurethane aqueous dispersions (PUDs) [15–17].

In addition to the primary reagents, polyols, and isocyanates, the manufacture of polyurethanes involves the strategic addition of components that have a significant influence on essential characteristics. These include density, porosity, material morphology, and the speed of chemical reactions. Among them, catalysts, chain extenders, crosslinkers, and surfactants stand out [15].

Catalysts play a crucial role in accelerating the reaction between isocyanates and polyols, reducing activation energy and improving process efficiency. This acceleration is vital to the economic and technical viability of production. Traditionally, organometallic catalysts have been widely used, with emphasis on tin-based compounds such as dibutyltin dilaurate (DBTDL) and dibutyltin diacetate (DBTDA) [15,18]. However, due to the toxicity of many of these compounds, there has been growing interest in less harmful alternatives, such as bismuth- and zinc-based catalysts, which offer similar performance with less environmental impact [15].

In addition to catalysts, chain extenders are low-molecular-weight compounds, usually terminated with hydroxyl or amine groups, that react with isocyanates to introduce rigid segments into the polymer structure. Their presence increases bond density and can reduce the material's flexibility [15].

Crosslinkers, characterized by functionality of at least 3, enable the formation of a three-dimensional network among the polymer chains. This crosslinking significantly increases the mechanical and thermal resistance of PU. Polyurethanes that are strongly crosslinked tend to exhibit thermosetting behaviour, while formulations with a lower degree of molecular interlocking result in thermoplastic materials. Finally, surfactants are added to ensure miscibility between the reagents and stabilize the morphology of the material during polymer formation [15,19].

The global PU market has shown steady growth over the years. Information indicates that the estimated value will be around USD 83.38 billion in 2024, with forecasts reaching USD 90.52 billion in 2025, representing a compound annual growth rate (CAGR) of 8.6%. This expansion is expected to accelerate, with forecasts indicating it will reach approximately USD 122.45 billion by 2029 [20].

As a result, more sustainable alternatives are being sought to meet this demand, driven by initiatives focused on sustainability, energy efficiency, and the adoption of greener industrial practices [19]. In this context, biobased polyurethanes emerge as a promising option for reducing the environmental impacts associated with traditional production. These materials use renewable raw materials, in whole or in part, instead of fossil-derived polyols, in accordance with sustainable development and circular economy guidelines [18].

2.4 Biobased polyurethane

With the growing demand for sustainable solutions, bio-based polyurethanes are emerging as promising alternatives to traditional petroleum-based products. The main difference lies in the origin of the polyol, which is produced from renewable sources such as vegetable oils (soybean, castor bean, palm, sunflower), sugars, starch, cellulose, glycerol, lignocellulosic waste, and animal-derived sources such as proteins and natural fats [18].

Figure 2 illustrates this, presenting examples of PU preparation using renewable raw materials. It shows various tactics for employing animal- or plant-based polyols, as well as the use of chain extenders. In addition, it emphasizes the primary industrial uses, such as coatings, adhesives, and antimicrobial materials [21].

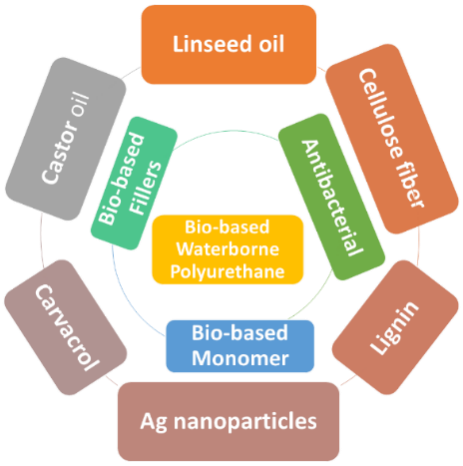

Figure 2 – Adapted - Illustration of the main routes for the preparation of waterborne polyurethane (WBPU) using renewable raw materials and different synthesis strategies [21]

To ensure reactivity with isocyanates in polyurethane manufacture, these natural raw materials are chemically modified to introduce hydroxyl groups. The use of renewable polyols significantly reduces the carbon footprint and dependence on fossil resources, without compromising, and in some cases even improving, characteristics such as flexibility, thermal resistance, and dimensional stability. However, each renewable energy source has its own advantages and disadvantages, making it necessary to choose the most suitable one for the intended application [15,18,19].

In this context, the use of bio-based polyurethanes has been encouraged by both regulatory requirements and market actions that value sustainability. This movement has encouraged technological progress and increased the availability of renewable raw materials, with a growing number of companies now offering biobased polyols and ready-made PU formulations, in line with the demands of various industrial sectors [18].

In recent years, large chemical companies have invested in developing and commercializing polyurethanes and polyols from renewable sources, seeking to meet the growing demand for sustainable solutions. Among the leading companies in the sector are BASF, Cargill, Emery Oleochemicals, Polylabs, and Synthesia Technology. These materials are developed with varying degrees of renewable content, which depend on the polyol source, the synthesis process, and performance requirements, as shown in Table 2.

Table 2 – Overview of commercially available biobased polyols, including suppliers, renewable content, chemical characteristics, and main applications

Company	Product	Bio-based content %	WM	Type	Source	Application/Benefit	Ref.
Basf	SOVERMOL® 1005	80 - 100	-	-	Oil and castor oil	Pipe Coating, ACE, General Industry, Wind power	[22]
Cargill	Priplast™ Family (some examples: 3238, 3294)	100	1000-3000	Polyester polyol (liquid)	Vegetable oil	Good adhesion even on low-polarity substrates, resistance to thermo-oxidation and hydrolysis, greater durability, and improved moisture protection	[23]
Synthesia Technology	BIO-HOOPOL 9110	90	2000	Saturated linear polyester polyols	Acids and glycols obtained from renewable sources	Adhesives, coatings, elastomers, shoe soles	[24]
	BIO-HOOPOL 11503	100					
Emery Oleochemicals	EMEROX® 14550	82	2000	Aliphatic	Based on renewable and naturally derived acids	Prepolymer: coatings, adhesives, sealants and elastomers	[25]
	EMEROX® 14803	95				Coatings, adhesives, sealants and elastomers	
Polylabs	Bio Polyols	51 - 83	-	-	By-products from forestry and recycled oils	Greener alternative for the polyurethane industry	[26]

These characteristics, such as controlled reactivity, low viscosity, and compatibility with water-emulsifiable processes, make these products a particularly suitable choice for PUD formulations.

As an example, Zhang et al. 2021 developed a PUD using renewable polyols, castor oil-glycerol-based WPU with a cross-linker, which showed exceptional performance in industrial coatings. Research indicates that these materials can have low toxicity, high flexibility, and chemical resistance, meeting performance requirements comparable to those of conventional petroleum-based formulations [27]. This example demonstrates that bio-based polyurethanes are not only commercially available but also have technically viable and promising large-scale applications [21,27].

2.5 Aqueous polyurethane dispersions

PUDs are a fundamental technology in the search for high-performance, environmentally friendly materials. These formulations, which use water as a dispersion medium rather than volatile organic solvents, significantly reduce pollutant emissions, making them innovative solutions for coatings, adhesives, textiles, synthetic leather, and films [4,28]. Their widespread adoption is driven by stricter environmental laws and industry demand for sustainable products that maintain technical performance.

They are called waterborne polyurethane and waterborne polyurethane-urea systems and have been growing in popularity as more sustainable alternatives to conventional systems that use organic solvents [13]. These materials enable a considerable reduction in environmental impacts without compromising technical performance, making them relevant to various applications [19,29].

Previous work developed within the same research framework, particularly the study conducted by Berto et al. (2024) [30], has already addressed the synthesis and characterization of PUDs. This study provided valuable insights into key parameters such as synthesis conditions, colloidal stability, and structure–property relationships in PUD systems. The results demonstrated how formulation variables influence dispersion stability and final material performance, contributing to the optimization of processing strategies. Building on these findings, the present work further explores the incorporation of bio-based polyols, aiming to enhance the sustainability of these systems while maintaining their functional performance.

These can be classified by their chemical composition and chain structure: waterborne polyurethane-urea dispersions (WBPUU) can comprise solely of polyurethane segments, or include additional urea units, resulting in greater mechanical strength and stability [33]. Another criterion concerns the surface charge of the particles, which can be anionic, cationic, or neutral. In addition, the particles can range in size from nanometres to micrometres [3,31].

In terms of properties, these dispersions have good colloidal stability and adjustable viscosity, characteristics that simplify their handling in multiple processes [32]. They also form continuous films that demonstrate excellent adhesion to various substrates, ensuring satisfactory performance in coatings, adhesives, and thin films without the need for major modifications to the basic PU formulation [29].

The production method plays a key role among the factors that affect the final quality of PUDs. The appropriate selection of the synthesis process directly affects the stability of the

dispersion, the final characteristics of the polymer, industrial viability, and even the ecological impact related to production [4].

The main methods used in the synthesis of PUDs are summarized in Table 3, which highlights their characteristics, advantages, and associated challenges. Additionally, in all approaches, the characteristics of the material are strongly affected by the chemical structure of the PU: the soft segments (originating from the polyol) offer flexibility, elasticity, and resistance to deformation, while the hard segments (derived from isocyanate and chain extenders) create rigid domains that ensure mechanical strength, thermal stability, and durability [33].

Table 3 – Main synthesis methods for aqueous polyurethane dispersions, including description, advantages, limitations, and environmental aspects

Method	Description	Advantages	Disadvantages	Environmental Aspect	Ref
Acetone process	Prepolymer is dissolved in acetone to reduce viscosity, hydrophilic emulsifier also acts as a chain extender, and phase inversion occurs after adding water.	Reproducible control of particle size and distribution to avoid viscosity issues.	Use of large amounts of acetone, adding an extra recovery/purification step.	Produces VOCs; need to recover solvent to reduce impact; less sustainable process.	[34,35]
Prepolymer process	NCO-terminated prepolymer (isocyanate + polyol + emulsifier); dispersed in water after neutralization; uses polar co-solvent (NMP) and sometimes acetone.	Allows polymers with higher molecular weight and suitable mechanical properties to be obtained.	Use of NMP (highly toxic, difficult to remove); dependence on organic solvents.	Strong environmental impact from NMP, restricted by legislation; need for replacement with greener routes.	[36,37]
Modified prepolymer process	Variation of the previous method; dissolution of the emulsifier in acetone with a neutralizing agent, eliminating NMP and using less acetone.	Avoids the use of NMP; reduces the amount of solvent required; produces dispersions with good properties.	It still depends on acetone in certain steps.	More environmentally friendly than traditional prepolymers, but not 100% solvent-free.	[36–38]
Solvent-free methods	Synthesis in the absence of organic solvents; hydrophilic extenders or excess isocyanate can be used as the reaction medium; dispersion in water under controlled conditions.	Elimination of organic solvents; shorter synthesis time and lower energy consumption; properties comparable to conventional routes.	Side reactions (NCO + H_2O) need to be controlled; requires process rigor.	Best environmental alternative: no VOCs, lower energy consumption and waste; aligned with green chemistry principles.	[39–41]

Among the described methods, the modified prepolymer process has been widely used in scientific studies, representing significant progress compared to the traditional process, as it eliminates the need for N-methyl-2-pyrrolidone (NMP) - a highly toxic and regulated solvent - and requires smaller amounts of acetone [4].

This approach allows the production of stable dispersions with satisfactory technical performance and is more aligned with the principles of green chemistry. In the research conducted by Sun et al. (2023), stable NMP-free PUDs were obtained, resulting in particles with a uniform size distribution. The films formed exhibited good mechanical resistance, high adhesion, and low VOC emissions, demonstrating the method's suitability for sustainable, large-scale industrial applications [38].

This example illustrates how the modified route combines environmental viability and technical performance, validating its consolidation as one of the most important synthesis routes for the production of PUDs. Thus, understanding the classification and properties of these dispersions is essential, as it determines their suitability for various industrial and sustainable applications.

In addition to the technical aspects, it is important to note that the global market for PUDs has been expanding steadily, reflecting growing appreciation for sustainable industrial solutions. In 2024, this market is estimated to have reached approximately US$ 2.42 billion, and projections indicate that it could reach US$ 3.46 billion by 2032, corresponding to a CAGR of 4.6% [42]. This expansion is the result not only of regulatory pressures, which encourage the reduction of VOCs, but also of growing social and corporate demand for cleaner and more environmentally responsible processes [43].

2.6 Relevance of PUDs in Sustainable Footwear Manufacturing

The footwear industry is a globally significant economic sector, with annual production exceeding 22 billion pairs in 2023. Although most production is concentrated in Asia, countries such as Brazil and Portugal also have a significant share [43]. This production chain encompasses various raw materials, such as leather, fabrics, rubber, and polymers, and is highly dynamic in terms of technological innovation and economic value creation [5].

Despite its economic relevance, the sector faces significant environmental challenges, primarily due to the use of solvent-based traditional adhesives and conventional PU, which release VOCs and generate waste throughout the production

process. These environmental impacts highlight the need for more sustainable alternatives in footwear manufacturing [5,32].

In response, the industry has intensified its sustainability initiatives, including using bio-based raw materials and recycled polymers for soles, replacing cork composites, developing alternative leathers, and adopting circular economy practices such as waste recycling and reverse logistics. Life cycle assessments (LCAs) highlight the importance of these measures by showing that traditional PU adhesives have a considerably larger environmental footprint than more innovative and sustainable alternatives [44,45].

Footwear production involves stages such as cutting, sewing, assembly, and finishing, providing several opportunities to apply sustainable technologies and serving as an important starting point for multiple research efforts. Among these practices, the replacement of solvent-based adhesives with aqueous dispersions, the use of water-based functional coatings, and the incorporation of solid waste into composites stand out. These solutions both drive technical advances and reinforce the sector's competitiveness and environmental responsibility [5].

In this way, advances in aqueous polyurethane dispersions and renewable inputs not only meet contemporary environmental demands but also point to a more resilient, competitive, and sustainable production model for the global footwear industry.

3 METHODOLOGICAL PROCEDURES

3.1 Materials

For the synthesis of aqueous dispersions, biodegradable polyols (Polycaprolactone) and bio-based polyols from two different suppliers were selected based on their characteristics and potential for sustainable use, as shown in Table 3. Other reagents and additives essential for the synthesis of PUDs were also used, as detailed in Table 4.

Table 4 – Characteristics of the polyols used in this work, including supplier, biobased content, molecular weight, viscosity, and chemical structure

Description	Supplier	Biobased Content (%)	Molecular Weight (g/mol)	Viscosity (mPa·s)	Appearance	Characterization
PCL 2000	INGEVITY	-	2000	385 (60°C)	Solid	Linear saturated polyester polyol
PCL 1000	INGEVITY	-	1000	-	Solid	Linear saturated polyester polyol
DIEXTER E50155	COIM GROUP	100%	2000	4200-5600 (Brookfield - 35°C)	Waxy solid	Linear saturated polyester polyol
DIEXTER E50274	COIM GROUP	100%	2000	450-750 (Brookfield - 80°C)	Solid	Linear saturated polyester polyol

Table 5 – List of reactants used in the synthesis of aqueous polyurethane dispersions, including their respective abbreviations and suppliers

Product	Abbreviations	Supplier
Isophorone diisocyanate	IPDI	Alfa Aesar
Dibutyltin dilaurate	DBTDL	Sigma-Aldrich
Dimethylol propionic acid	DMPA	Fluka
Triethylamine	TEA	Fluka
Dry acetone	-	Panreac
1,2-ethylene diamine	EDA	Panreac

3.2 PUD Synthesis

The synthesis of PUDs was carried out in four main stages: reaction, emulsification, neutralization, inversion, and chain extension. The process was conducted in a 500 mL jacketed reactor equipped with temperature control and a mechanical stirrer, operating at a scale of 100 g.

In the first stage (reaction), the reactor was assembled and loaded with the polyol, followed by verification of the agitator's operation and temperature control. Next, the DBTDL catalyst was added. The mixture was heated to 80 °C while stirring at 200 rpm. The previously weighed isocyanate was added dropwise using a syringe. After 15 minutes, a sample was taken, and the residual NCO content was determined by titration according to ASTM D 2572-97, which involves reacting the sample with a DBA/toluene solution under controlled conditions and then titrating it with HCl (1 M). The sample was subsequently cooled to 55 °C to begin the next step. This reaction time is not fixed; it was defined by the research group as an optimized condition that may vary depending on the polyol used and is maintained until the desired theoretical NCO conversion is reached, generally around 60%.

In the second phase (emulsification and neutralization), the temperature was maintained at 55 °C and a solution containing DMPA (5% polyol weight-basis), dry acetone (25 mL), and TEA (in the amount required to neutralize 95% of the carboxylic acid (COOH) groups in the DMPA) was gradually added. The mixture was stirred at 200 rpm for 15 minutes, after which a sample was collected and cooled to 25 °C. If an increase in viscosity was observed, acetone was added to dilute the mixture and decrease the viscosity.

The third stage (inversion) began with the removal of the thermocouple and an increase in stirring speed to 500 rpm. The peristaltic pump was set to a flow rate of 5 mL/min and the addition of deionized water was initiated in a smaller amount. At this stage, a temporary increase in motor power was observed, which is typically associated with the phase inversion of the system. Once this transition occurred, the water flow was gradually increased until reaching the total addition of 120 mL at 25 °C over 30 minutes. After this, a sample was then collected, and the reactor was heated to 35 °C for the final stage.

In the fourth stage (chain extension), at 35 °C and with stirring at 200 rpm, 20 mL of deionized water and EDA were added, this was calculated according the conversion after phase inversion in the last titration, using the peristaltic pump set to a constant flow rate 0.3 mL/min and with only one tube. The process was maintained for 2 hours. After, the stirring and heating were turned off, and the final sample was collected before dismantling the reactor.

3.3 Characterization of the PUDs

The properties of the PUDs were evaluated at different levels: directly in the dispersions (biobased content, pH, solids content, viscosity, particle size, zeta potential, and electrolyte stability), in the films (DSC and TGA), and in tests related to potential industrial applications (DMA for viscoelastic behaviour, T-peel test for adhesive performance, WVP, and water absorption and desorption).

3.3.1 BIOBASED CONTENT

The renewable content of the dispersions was estimated from the biobased fraction of the polyols, as specified in their technical datasheets. This calculation was performed

using Equation (1), where *P* is the mass of the polyol used in the reaction (g), *BC* is its biobased content (%), and m_t is the total mass of all reagents used in the formulation (g).

$$Biobased\ content\ (\%) = \frac{P \times BC}{m_t} \quad (1)$$

3.3.2 pH

The pH was determined according to EN 1245:1998, using a calibrated pH meter (WTW InoLAB PH 720 PH Meter, Germany). The electrode was immersed directly into the sample, and the value was recorded once the reading stabilized in triplicate.

3.3.3 SOLIDS CONTENT

The solids content was determined by weighing 1.00 g of dispersion into a pre-weighed Petri dish, which was then placed in an oven at 100 °C for 2 h. After drying, the sample was transferred to a desiccator until reaching room temperature and weighed again. The solids content was calculated using Equation (2), where m_i and m_f represent the initial and final masses, respectively.

$$Solid\ content\ (\%) = \frac{m_f}{m_i} \times 100 \quad (2)$$

3.3.4 VISCOSITY

The viscosity of the PUD was assessed using a Visco Star viscometer manufactured by Fungilab (Brookfield - Barcelona, Spain), coupled with an Electro Temp thermostatic bath to maintain a constant temperature. For this purpose, 8 mL of the sample was added to the container and homogenized with the TL5 spindle for 1 minute, with readings recorded every 10 seconds. The final viscosity value was obtained from the average of three consecutive measurements.

3.3.5 STATISTICAL ANALYSIS

The statistical analysis of the results (pH, solids content and viscosity) obtained from the dispersion characterisation was conducted using Minitab Statistical Software, version 22. Model adequacy was verified through analysis of variance (ANOVA) to identify significant differences between the PUDs. When ANOVA indicated relevant differences, Tukey's test was applied at a significance level of $p \leq 0.05$ and a 95% confidence interval (CI) to assess which means showed significant variations.

3.3.6 PARTICLE SIZE AND ZETA POTENTIAL

The average particle size and zeta potential of the PUDs were determined using a Malvern Zetasizer Ultra - Blue from Worcestershire, UK. For analysis, the sample was diluted in distilled water to avoid multiple scattering effects. Then, the diluted dispersion was transferred to the appropriate measurement cell (DTS107) for aqueous systems.

Measurements were carried out in dynamic light scattering (DLS) mode to determine particle size and in electrophoretic mobility mode to determine zeta potential. Mean values and standard deviations were then obtained based on three consecutive readings. The resulting data were processed to generate graphs of particle size distribution and zeta potential variation.

3.3.7 ELECTROLYTE STABILITY

Electrolyte stability was evaluated following a method adapted from Pérez-Limiñana et al. (2005). Each test consisted of adding a 2 M sodium chloride (NaCl) solution to 5 mL of PUD previously diluted in distilled water at a 1:1 (v/v) ratio, until visible coagulation of the dispersion occurred. The volume of NaCl solution required to reach this point was recorded.

3.3.8 FILM PREPARATION

To obtain PUD films, 6.24 g of dispersion was poured into Teflon® molds. The samples were left to dry under ambient conditions for seven days to allow water to evaporate and solid films to form. After this period, the films were carefully removed from the molds and used for characterization analyses, as well as to evaluate the final appearance of the film.

3.3.9 THERMOGRAVIMETRIC ANALYSIS

The thermal stability of the samples was determined by thermogravimetric analysis (TGA) to identify the thermal degradation profile and mass loss as a function of temperature. The analyses were performed on a TG model 20F3 Tarsus device, using approximately 7 mg of sample packed in aluminium crucibles. Heating was conducted from 30 °C to 800 °C at a rate of 10 °C/min in an inert nitrogen atmosphere. The thermograms obtained were processed using Netzsch Proteus Thermal Analysis software, version 5.2.1.

3.3.10 DIFFERENTIAL SCANNING CALORIMETRY

The thermal behavior of the films was evaluated by Differential Scanning Calorimetry (DSC) to determine the glass transition temperature (Tg) and melting temperature (Tm). The measurements were performed using a Netzsch DSC 204 F1 Phoenix (Selb, Germany) equipped with an electric cooling system. Samples weighing approximately 7–8 mg were placed in aluminium crucibles and subjected to controlled heating, ranging from -60 °C to 300 °C, at a rate of 20 °C/min, under a continuous flow of nitrogen.

3.4 Screening of potential applications

3.4.1 POTENTIAL AS ADHESIVES

The viscoelastic behaviour and adhesive performance of the polyurethane dispersions were evaluated using Dynamic Mechanical Analysis (DMA), a NETZSCH DMA 303 Eplexor (NETZSCH Gerätebau GmbH, Germany, 2024), which ensured strict control of temperature and testing conditions throughout all analyses.

Dynamic Mechanical Analysis (DMA) was performed over the temperature range −50 °C to 60 °C at a heating rate of 2 K/min and a frequency of 1 Hz. Rectangular PUD film specimens (20 mm gauge length × 3.5 mm width × 0.5 mm thickness) were tested at deformation amplitudes of 0.01 or 0.02 mm. The storage modulus (E′), loss modulus (E″), and damping factor (Tan δ) were recorded as a function of temperature to evaluate the viscoelastic properties of the materials.

The adhesive performance was assessed using T-peel tests conducted in accordance with ASTM D1876 on the same DMA equipment. Test specimens were prepared by bonding two substrates with the aqueous dispersion to form T-shaped adhesive joints, as shown in Figure 3. The dispersion was applied uniformly over a 5 mm bonding area and the coated substrates were dried for two hours prior to bonding. To reactivate the adhesive, the samples were heated to 50 °C with a hot-air gun (PHLGD 2000 D5, Parkside, Germany), and the temperature was controlled with an external thermometer. After reactivation, the substrates were brought into contact and pressed using a hydraulic press for 30 seconds at approximately 1 bar to ensure proper adhesion. The bonded specimens had approximate dimensions of 15 mm in length, 7–8 mm in width, and a total thickness of 1.5–2.0 mm.

During the T-peel test, the force required to separate the joint was continuously recorded as a function of displacement, with a loading rate of 0.2 N/s. The peel strength was determined from the average force measured in the stable region of the force–displacement curve.

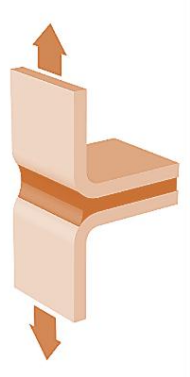

Figure 3 – Representation of the T-peel test configuration used to evaluate the adhesive performance of bonded samples[46]

3.4.2 POTENTIAL AS COATINGS

Water vapour permeability (WVP) was determined in accordance with the ASTM E96–95 standard [47]. Circular permeation cells with a diameter of 3 cm were filled with distilled water to within ¾ of their volume and sealed with test films to allow for vapor transfer only through the sample.

The assembled cells were weighed initially, then placed in a desiccator containing silica gel to maintain a low-humidity environment. The cells were weighed at 1-hour intervals for 8 hours to monitor, and a final reading was performed 24 hours after the first measurement, to determine the mass of water vapour transmitted across the film. The water vapour transmission rate (WVTR) was calculated from the slope of the linear region of the mass change-time plot using Equation 5.

$$WVTR = \frac{G}{T \times A} \qquad (5)$$

$G =$ weight change (g)

$T =$ time (h)

$A =$ test area (cup mouth area), m^2

Where G/t expresses the weight loss per unit of time (g/h), and A is the area of the vessel's mouth (m^2). The obtained WVTR values were used to calculate the WVP using Equation 6.

$$WVP = \frac{WVTR \times Th}{\Delta P} \quad (6)$$

$Th =$ film thickness (mm)

$\Delta P =$ partial pressure difference between the two sides of the film(kPa)

To calculate ΔP, the relative humidity was assumed to be 100 % on the inner surface of the film and 0 % on the outer surface (25 ◦C).

3.4.3 POTENTIAL AS AGGLOMERATES

The cork-based composites were manufactured using a hydraulic press equipped with heated platens and hot pressing (Figure 4). 10 grams of cork were used for each sample (granulometries 0.5 – 1 mm), while the PUD proportion was fixed at 30% (w/w relative to the cork mass). First, the cork was weighed into a metal vessel, then the required amount of PUD was added. The components were mixed mechanically at 1000 rpm for 10 minutes using an IKA EUROSTAR 20 High Speed Digital mechanical stirrer (IKA-Werke GmbH & Co. KG, Staufen, Germany) equipped with a Teflon® paddle stirrer to ensure uniform dispersion. The resulting blend was placed in a mold lined with vegetable paper to prevent the PUD from adhering to the mold surfaces. After closing the mold, which had a thickness limitation of 4 mm, it was subjected to 15 bar of pressure at 135 °C for 2 minutes in the hydraulic press, with the sample curing time also occurring in the press. The samples were then stored at ambient temperature for one week before testing.

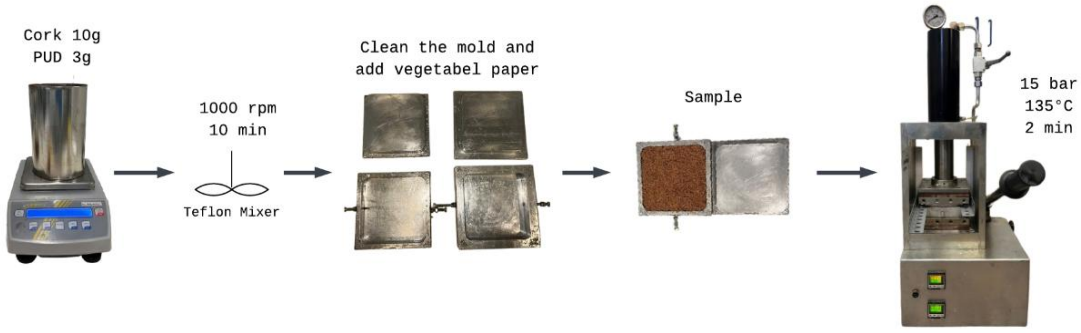

Figure 4 – Representation of the manufacturing process of cork-based composites using aqueous polyurethane dispersions

To inspect the performance of the cork agglomerates as shoe insoles, water absorption and desorption were determined for the produced composites.

The water absorption and desorption of the composite samples were evaluated in accordance with ISO 22649:2016. The specimens were cut into 50 mm × 50 mm samples and weighed initially (m_i). These were then immersed in distilled water for six hours. After this time, they were removed, surface-dried and weighed again to obtain the final mass (m_f).

For the desorption step, the samples were dried at room temperature for sixteen hours and then weighed again (m_r). Water absorption (W_a) and desorption (W_d) were then calculated using Equations (3) and (4), respectively. According to ISO/TR 22649, adequate performance is achieved when water absorption exceeds 70.0 mg/cm² and desorption is at least 60.0%.

$$W_a\ (\mathrm{mg/cm^2}) = \frac{m_f - m_i}{sample\ area} \quad (3)$$

$$W_d\ (\%) = \frac{(m_f - m_r)}{(m_f - m_i)} \times 100 \quad (4)$$

4 RESULTS AND DISCUSSIONS

Different PUD formulations were developed using both biobased and synthetic polyols, with seven dispersions synthesized from the biobased polyols DIEXTER E50155 and DIEXTER E50274, and two prepared from the synthetic and biodegradable polyols PCL 2000 and PCL 1000. Immediately after synthesis, all dispersions exhibited a homogeneous, fluid appearance, with visual characteristics ranging from translucent to milky white, for example as illustrated in Figure 5. This variation in appearance is associated with differences in the final particle size achieved during synthesis.

However, after approximately 6-8 weeks of storage, three dispersions showed phase separation, indicating a loss of colloidal stability over time: DTX155_1, DTX274_1, and DTX274_3. This behaviour suggests that, despite the initially homogeneous aspect, certain formulations were unable to maintain long-term stabilization under the tested conditions.

Figure 5 – PUD sample showing its visual appearance after synthesis

All samples presented a biobased content higher than 50% for the polymer dispersed in water. The biobased content of the produced dispersions ranged from approximately 68.47% to 68.71%, indicating a highly consistent renewable fraction across the formulations. In contrast, the biobased content of DTX274_2 could not be determined, as this dispersion became unstable during the synthesis, developing a gel-like structure, as shown in Figure A1, Appendix A. Detailed information regarding biobased content, synthesis conversion, water content, acetone consumption, and chain extension conditions is summarized in Table A1.

Among the synthesized formulations, DTX155_2, DTX274_3, DTX274_4, and DTX274_5 were prepared using a higher water volume (170 mL) during the inversion step phase. When a lower volume (120 mL) was employed, the resulting dispersion showed reduced stability after a few days, as illustrated in Figure A2. This behaviour may be related to the intrinsic hydrophobicity of bio-based polyols, which can hinder their dispersion in aqueous media.

Some processing parameters were adjusted during the development of the formulations in response to stability issues observed in the initial dispersions. Early formulations prepared with 60% chain extender exhibited phase separation and formed a two-phase system after synthesis, indicating insufficient colloidal stability. This behaviour was attributed to excessive chain extension prior to complete dispersion, which may have increased the molecular weight and promoted microphase separation, hindering effective emulsification [48,49]. To improve stability, the amount of chain extender was reduced to 40% in samples DTX155_2, DTX274_4 and DTX274_5. This modification

produced more stable dispersions, demonstrating the importance of controlling chain growth before and during phase inversion for achieving stable PUD systems.

In addition, the formulations DTX274_4 and DTX274_5 differed only in the initial reaction temperature: 80 °C and 90 °C, respectively. The higher temperature was required for DTX274_5 due to the relatively high melting temperature of the polyol, ensuring complete melting and homogeneous incorporation into the polyurethane structure.

The volume of acetone added during synthesis also differed between the PUDs. PCL_1 required 20 mL; PCL_2, DTX155_1, and DTX274_1 required 25 mL each. Higher amounts of acetone were necessary for DTX155_2 (60 mL), DTX274_4 (75mL), DTX274_2 and DTX274_5 (100 mL), DTX274_3 (125 mL). These volumes were adjusted in response to the observed viscosity during synthesis. More viscous systems required higher acetone contents to ensure successful phase inversion. Acetone served as a temporary solvent that controlled the viscosity during the formation of internal crosslinking networks throughout the polymerization process [50]. However, given the process's sustainability orientation, the presence of acetone in the final formulation is undesirable. Thus, at the end of the synthesis, the dispersions were subjected to solvent removal on a rotary evaporator to remove excess acetone. On an industrial scale, the recovered acetone could be collected and reused, making the process more sustainable and resource-efficient.

Furthermore, dispersions that demonstrated destabilization during storage, DTX155_1, DTX274_1, and DTX274_2, are excluded from the subsequent analyses. Only the formulations that maintained long-term colloidal stability are considered in the subsequent analysis of physicochemical properties and performance, ensuring that conclusions are based on representative and reliable samples.

4.1 pH, Viscosity, and Solids Content

The results of the dispersions prepared with PCL 2000, PCL 1000, DIEXTER E50155, and DIEXTER E50274 characterization, pH, viscosity, and solids content are summarized in Table 6.

Table 6 – Physicochemical properties of the synthesized dispersions: pH, viscosity, and solids content

Sample	pH	Viscosity (mPa.s)	Solids Content
PCL_1	7.49 ± 1.53E-02	19.39 ± 2.27E-04	39.04% ± 1.99E-04
PCL_2	7.63 ± 5.77E-02	17.12 ± 5.37E-02	38.60% ± 1.14E-03
DTX155_2	7.67 ± 5.77E-03	14.84 ± 1.66E-02	36.73% ± 1.80E-03
DTX274_4	7.71 ± 5.77E-03	16.17 ± 1.40E-01	33.97% ± 7.02E-03
DTX274_5	7.76 ± 3.46E-02	15.77 ± 7.71E-03	32.61% ± 2.11E-03

Values are expressed as ± mean standard deviation.

All dispersions exhibited pH values within a narrow range near neutrality, consistent with the experimentally observed stability. This trend is consistent with studies on anionic waterborne polyurethane dispersions, in which the introduction of ionic centres shifts the pH to the neutral to slightly basic range, thereby contributing to electrostatic stabilization of the colloidal system [3,50].

In addition, the measured pH values, which are typically in the range of 7 to 10, are in good agreement with those reported in the literature for water-based anionic polyurethane dispersions. This behaviour also indicates that the chain extension reaction was efficiently controlled, which is associated with chain growth and increased viscosity. On the other hand, a decrease in pH can compromise the ionization of the stabilizing groups, thereby reducing electrostatic repulsion and dispersion instability [50].

The viscosity values varied significantly between formulations, reflecting differences in chemical composition, degree of chain extension, and volume of solvent used during synthesis. The PCL_1 and PCL_2 dispersions exhibited relatively high viscosities (17–19 mPa.s), which is consistent with the more homogeneous and predictable nature of synthetic polyol, as well as with the lower structural complexity of the system. In addition, the longer chain length in this formulation may have contributed to the formation of a more intertwined polymer network, resulting in greater resistance to flow, even at relatively low solids contents [49].

Samples made with biobased polyols DTX155_2, DTX274_4, and DTX274_5 exhibited intermediate viscosities of approximately 14–16 mPa·s. This suggests a balanced relationship between chain growth and effective particle dispersion after phase inversion [51]. These values suggest that the synthesis conditions enabled sufficient molecular weight development while maintaining good colloidal stability.

Figure 6 shows the variations in solids content and viscosity. The solid content of the polyurethane dispersions ranged from around 32% to 40%, reflecting variations in polyol composition, reaction progression, and the extent of chain extension. Generally,

higher solid content was associated with increased viscosity, due to the greater concentration of polymer particles and intensified interparticle interactions within the aqueous phase, but the DTX155_2 sample was different from the others.

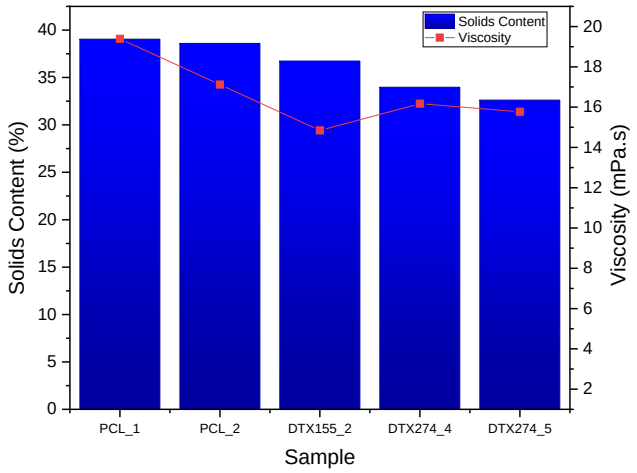

Figure 6 – Variation of solids content and viscosity for the different aqueous polyurethane dispersions

According to the literature, stable polyurethane dispersions typically exhibit solid contents between 30% and 40% [51,52]. The analysed samples fall within this range, with solids content above 32% and viscosities between 15 and 19 mPa·s. This behaviour indicates the formation of a sufficiently developed polymer network that maintains effective colloidal stabilization while allowing relatively high solid loads without excessive flow resistance. Such a balance is particularly advantageous for adhesive applications, as it ensures adequate coating performance while reducing the amount of water that must be evaporated during processing.

ANOVA was performed to evaluate whether the differences observed in pH, viscosity, and solids content among the PUD formulations were statistically significant. When significant differences were identified, Tukey's test was applied to compare the means at a 95% confidence level. The results of the statistical analysis are presented in Table 7.

Table 7 – Statistical analysis results (ANOVA and Tukey test) for pH, viscosity, and solids content

	pH		Viscosity		Solids	
Sample	**Group**	**CI of 95%**	**Group**	**CI of 95%**	**Group**	**CI of 95%**
PCL_1	D1	(7.65; 7.69)	A2	(19.33; 19.44)	A3	(38.41; 39.65)
PCL_2	C1	(7.68; 7.73)	B2	(17.03; 17.14)	A3	(37.98; 39.22)
DTX155_2	B1. C1	(7.74; 7.78)	E2	(14.79; 14.89)	B3	(36.11; 37.35)
DTX274_4	B1	(7.47; 7.52	C2	(16.12; 16.22)	C3	(33.35; 34.59)
DTX274_5	A1	(7.61; 7.65)	D2	(15.72; 15.83)	C3	(31.98; 33.22)

Each group comprises samples that are statistically similar to one another, meaning their mean values do not differ significantly at the 95% confidence level. Groups were defined based on Tukey's test, in which samples sharing the same letter are not significantly different.

In terms of pH, PCL_2 is in a different group, but DTX155_2 is in the same statistical group as them and DTX274_4, suggesting similar values close to neutrality. PCL_1 formed a different group and DTX274_5 exhibited slightly higher pH values. Regarding viscosity, the samples are dissimilar, so each one is in a different group. For solid content: PCL_1 and PCL_2 belong to the same statistical group, while DTX155_2 is alone with no corresponding group. This confirms that variations in composition significantly affect the final polymer concentration in the dispersions.

4.2 Zeta potential

The zeta potential results showed that all dispersions had negative surface charges, confirming electrostatic stabilization of the systems (Table 8). According to the literature, zeta potential is a key parameter that governs the stability of colloidal dispersions. Absolute values higher than - 35 mV are generally considered to be a base requirement for stable colloids [3]. Systems with values around −50 ± 10 mV typically exhibit excellent colloidal stability.

Table 8 – Zeta potential values of the synthesized dispersions

Sample	Zeta potencial (mV)
PCL_1	-61.54 ± 3.19E+00
PCL_2	-60.13 ± 1.03E-01
DTX155_2	-47.94 ± 9.96E-01
DTX274_4	-48.63 ± 2.48E-01
DTX274_5	-48.38 ± 7.70E-01

Values are expressed as ± mean standard deviation.

PCL_1 and PCL_2 exhibited the highest absolute values at −61.54 mV and −60.13 mV, respectively, indicating very strong electrostatic repulsion between particles and, consequently, excellent stability.

DTX155_2 (−47.94 mV), DTX274_4 (−48.63 mV), and DTX274_5 (−48.38 mV) exhibited slightly lower absolute values but remained well above the 35 mV threshold, indicating stable dispersions.

Overall, all samples demonstrated zeta potential values consistent with highly stable colloidal dispersions, confirming that the electrostatic stabilization mechanisms

were effective and that variations in anionic content did not compromise the overall stability.

4.3 Particle size

The particle size distributions of the developed polyurethane dispersions were evaluated in terms of intensity, volume and number distributions. The average particle sizes obtained for intensity are presented in Table 9.

Table 9 – Particle size results of the synthesized dispersions obtained by DLS

Sample	Particle size (nm)
PCL_1	100.2 ± 4.02E-01
PCL_2	198.2 ± 1.33E+00
DTX155_2	202.3 ± 4.16E+01
DTX274_4	178.7 ± 1.18E+00
DTX274_5	228.8 ± 4.09E+00

Values are expressed as ± mean standard deviation.

Analysis of the particle size distribution curves indicates predominantly unimodal behaviour in the number distributions, Figure 7, suggesting relatively uniform populations of particles in terms of count. However, differences become more evident in the volume distributions, Figure 8, where broader peaks and slight asymmetries are observed for the biobased samples. This indicates the presence of larger particles that disproportionately influence the volume-weighted mean diameter. The individual figures for each sample can be found in Appendix B, which shows how volume and particle size number behave.

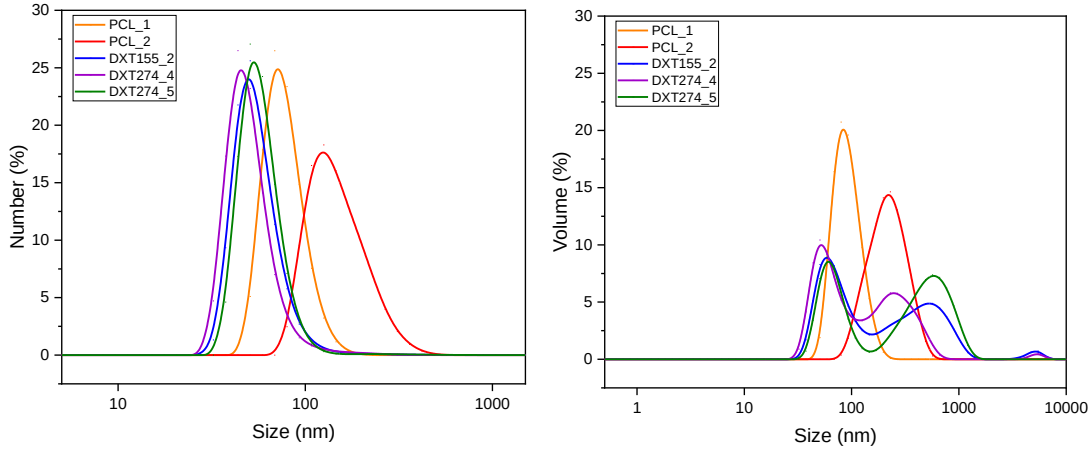

Figure 7 – Particle size distribution of the dispersions obtained by DLS: (a) number-based distribution and (b) volume-based distribution.

The significantly smaller particle size observed for PCL_1 suggests a more efficient dispersion process. This may be due to the particles being more hydrophilic,

which favours their stabilisation in an aqueous medium. However, as can be seen from the graph, the PCL_2 mixture showed a difference due to its molecular weight.

Although DTX274_5 was synthesized at a higher initial reaction temperature than DTX274_4, it exhibited a larger average particle size. This behaviour may be associated with the influence of reaction temperature on prepolymer viscosity and phase separation prior to dispersion. In that case, it would ultimately affect droplet breakup during phase inversion, thereby making the particle larger.

The particle size of the PUD is strongly influenced by structural and compositional parameters, including the relative content of hard and soft segments, molecular weight, the nature of the chain extender, emulsifier composition, and the degree of neutralization. The literature consistently reports that more hydrophobic polyurethane systems tend to form larger particles, as their lower affinity for water promotes faster aggregation during dispersion formation [32,38].

The presence of hydrophilic functional groups leads to smaller particles, a higher particle density, and a greater surface-to-volume ratio, which can promote further reactions at the particle surface. However, smaller particles can also increase dispersion viscosity due to swelling effects and electroviscous interactions within the electric double layer; this behaviour is consistent with the previously observed [49].

4.4 Electrolyte stability

The results obtained from the electrolyte stability test are presented in Table 10. The stability of dispersions in aqueous media is influenced by several factors, including molecular structure, ionic group content, polymer concentration, and temperature. In particular, the amount and distribution of ionic groups along the polymer backbone play a crucial role in maintaining sufficient surface charge to counterbalance attractive forces between particles [53].

Table 10 – Electrolyte stability of the dispersions expressed as the volume of NaCl solution required to induce coagulation.

Sample	NaCl (mL)
PCL_1	19
PCL_2	36
DTX155_2	10
DTX274_4	42
DTX274_5	42

It was observed that DTX274_4 and DTX274_5 exhibited the highest stability, requiring 42 mL of NaCl solution to induce destabilization. PCL_2 also showed relatively high resistance, destabilizing at 36 mL. In contrast, PCL_1 destabilized at 19 mL, while DTX155_2 presented the lowest stability, with coagulation occurring after the addition of only 10 mL of NaCl solution.

The electrolyte stability test provides insight into the robustness of the colloidal dispersion under increased ionic strength. The addition of salts compresses the electrical double layer, reducing electrostatic repulsion and potentially leading to particle aggregation and coagulation. Studies have shown that the effect of electrolyte concentration on colloidal stability can be explained by Derjaguin–Landau–Verwey–Overbeek theory, in which the balance between van der Waals attraction and electrostatic repulsion determines whether a dispersion remains stable in the presence of salts [54]. Furthermore, research on waterborne polyurethane systems has shown that the presence and distribution of ionic groups can enhance stability and influence resistance to electrolyte-induced destabilization [55].

4.5 Characterization of the PUDS films

The films obtained from the dispersions showed only minor visual differences between the formulations. It was expected that materials with a higher solids content and a higher degree of crystallinity would present greater opacity due to increased particle concentration during film formation [56]. However, while some variations in transparency were observed, this assumption was not strictly followed, mainly due to the crystallization tendency of the polyols used in the formulation.

Although the PCL based films had a relatively high solids content, they were more translucent than the other formulations. In contrast, the DTX based films appeared more opacity overall. Within this group, the films produced with DTX155 were more flexible and malleable, exhibiting mechanical behaviour similar to that of the PCL based samples.

Conversely, the DTX274 formulations resulted in films that were markedly more rigid and brittle. These samples were extremely fragile, which compromised their suitability for applications such as footwear adhesives. Figure 8 illustrates these differences, while the remaining films are presented in Appendix C.

Figure 8 – Films - PCL_1 | DTX155_2 | DTX274_1

4.5.1 THERMOGRAVIMETRIC ANALYSIS

To evaluate the thermal stability and degradation behaviour of the films obtained from the polyurethane dispersions, TGA was performed. The degradation temperatures (Temp) and corresponding mass loss percentages were determined from the derivative thermogravimetric (DTG) curves, which provide a clearer indication of the maximum degradation rate at each decomposition stage.

Figure 9 shows the DTG curves for all formulations, clearly distinguishing the mass loss events. The quantitative results, including the degradation temperatures, the percentage mass loss for each degradation stage, and the residual mass at the end of the analysis, are summarised in Table 13. The complete TGA and DTG curves for each sample are shown in Appendix E (Figures E1–E3).

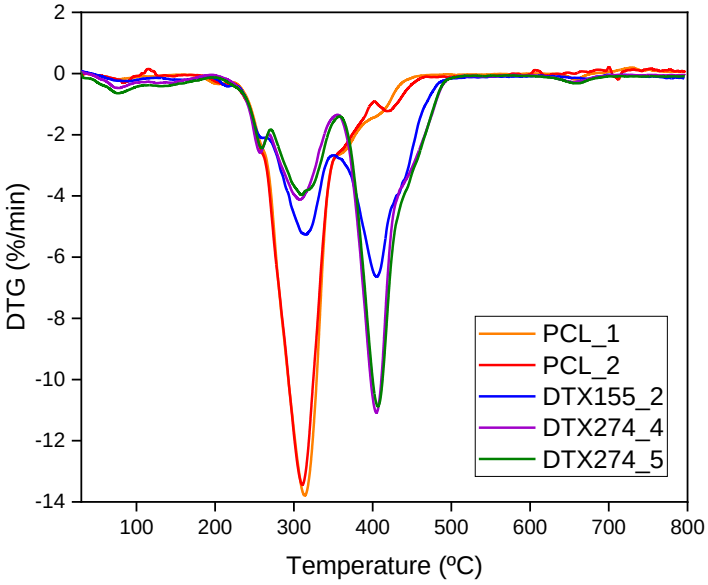

Figure 9 – DTG curves of PCL, DTX155, and DTX274 samples, showing the rate of mass loss as a function of temperature.

Table 11 – TGA results of polyurethane samples, including degradation temperatures and mass loss behaviour.

Peak	**1**		**2**		**3**		
Sample	**Temp (C°)**	**Mass Loss (%)**	**Temp (C°)**	**Mass Loss (%)**	**Temp (C°)**	**Mass Loss (%)**	**Residual (%)**
PCL_1	315.0	78.42	398.0	14.24	-	-	5.49
PCL_2	311.0	85.99	418.1	4.79	-	-	5.49
DTX155_2	314.6	36.87	405.4	47.68	-	-	9.28
DTX274_4	256.8	6.87	306.2	24.78	405.1	59.94	1.53
DTX274_5	258.9	6.94	306.8	25.02	406.9	60.12	1.52

The PCL-based samples exhibited a two-step degradation profile. The first and most significant stage of degradation occurred at approximately 311–315 °C, with a higher mass loss of 78.42% and 85.99% for PCL_1 and PCL_2, respectively. This stage is associated with the thermal decomposition of the polyurethane backbone, primarily involving the degradation of urethane linkages and soft segment structures. However, an initial mass loss below approximately 100 °C is commonly attributed to the release of physically adsorbed water, residual solvents, and other low-molecular-weight volatile species that remain in the film [57]. The second stage, which occurred between 398 °C and 418 °C, was characterized by lower mass losses (14.24% for PCL_1 and 4.79% for PCL_2), and is generally attributed to the breakdown of thermally more stable structures and carbonaceous residues. Both samples exhibited similar residual masses (5.49%).

On the other hand, DTX155_2 also exhibited a two-step degradation behaviour, but with a more balanced mass distribution between the two stages, as illustrated by the curve in Figure 11. The first degradation peak occurred at 314.6 °C, resulting in a mass loss of 36.87%, while the second peak at 405.4 °C accounted for a higher mass loss of 47.68%. This more evenly distributed degradation profile suggests differences in segment organization compared to PCL systems.

The DTX274-based formulations (DTX274_4 and DTX274_5) displayed a more complex, three-step degradation mechanism. An initial degradation event was observed at approximately 257–259 °C, with a relatively small mass loss of 6.9%. This early stage may be associated with the degradation of less thermally stable structures or residual low-molecular-weight species. The second stage of degradation occurred at around 306 °C, with a mass loss of approximately 25%. This was followed by a major peak of degradation near 405–407 °C, accounting for almost 60% of the total mass loss. These results indicate

a multi-stage decomposition mechanism reflecting a more heterogeneous structural organization in the DTX274 systems.

DTX155_2 exhibited the highest residual mass (9.28%), while DTX274_4 and DTX274_5 showed the lowest residual masses (~1.5%), indicating more complete thermal decomposition under the applied conditions.

4.5.2 DIFFERENTIAL SCANNING CALORIMETRY

The thermal behaviour of the synthesized films was evaluated by DSC. Thermograms obtained during the first and second heating scans were analysed to determine the melting temperature (T_m), and melting enthalpy (ΔH_m). T_m values were identified at the maximum of the endothermic transitions. The melting enthalpies were calculated by integrating the area under each endothermic peak. The obtained thermal parameters are summarised in Table 12 and the respective graphs for each sample are in Appendix D.

Table 12 – Thermal properties of polyurethane films obtained by DSC, including glass transition and melting temperatures

Sample	**T_{m1} (°C)**	**ΔH_{m1} (J/g)**	**T_{m2} (°C)**	**ΔH_{m2} (J/g)**	**T_{m3} (°C)**	**ΔH_{m3} (J/g)**
PCL_1	213 - 267	24.45	-	-	-	-
PCL_2	216.2 - 232.7	8.57	-	-	-	-
DTX155_2	46.3 - 203.8	73.94	213.1 - 233.6	17.78	-	-
DTX274_4	40.3 - 62.5	47.14	68.5 - 81.4	7.64	50.9 - 57.1	51.73
DTX274_5	42.5 - 59.4	62.84	66.3 - 76.5	8.05	39.5 - 59.6	54.39

The melting transitions revealed significant differences between the samples, indicating variations in the crystalline organization of the polymer matrix [58,59]. The PCL_1 and PCL_2 exhibited single melting events within high temperature ranges (213–267 °C and 216–233 °C, respectively) and had moderate melting enthalpies (24.45 and 8.57 J/g, respectively). These transitions are associated with the melting of crystalline domains derived from the polyester soft segment [59].

In contrast, the DTX155 and DTX274 samples displayed more complex melting behaviour, with multiple endothermic events observed in several formulations. DTX155_2 exhibited two melting transitions, suggesting the presence of crystalline domains with varying degrees of structural organization [59].

The DTX274 series exhibited the most complex thermal profiles. DTX274_4 and DTX274_5 exhibited up to three melting events, which suggests the presence of multiple crystalline populations. The first melting transition, which is typically observed between

40 and 60 °C, is attributed to less stable or thinner crystalline domains. The second transition, which occurs between approximately 66 and 81 °C, may be related to more ordered or thicker crystalline structures. In some cases, an additional melting event occurred during the second heating cycle, indicating structural reorganization and recrystallization phenomena during thermal treatment [58].

4.6 Potential applications

4.6.1 ADHESIVES

For the adhesive application, leather specimens were prepared under the same experimental conditions, with each dispersion acting as the bonding agent. Following the same procedure to ensure comparability between formulations, the substrates were coated, dried, thermally reactivated and pressed. Despite identical preparation conditions, differences in bonding performance were observed among the samples, as reflected in the T-peel strength results. Adhesive performance was evaluated through T-peel tests, while the viscoelastic behaviour of the materials was analysed using films obtained from the dispersions by DMA.

The figure 10 shows the tan δ curves of the polyurethane films obtained by DMA in the temperature range from −60 °C to 50 °C. Tan δ, the damping factor defined as the ratio of the loss modulus (E″) to the storage modulus (E′), represents a material's ability to dissipate mechanical energy. It is commonly used to determine the Tg which corresponds to the tan δ peak maximum.

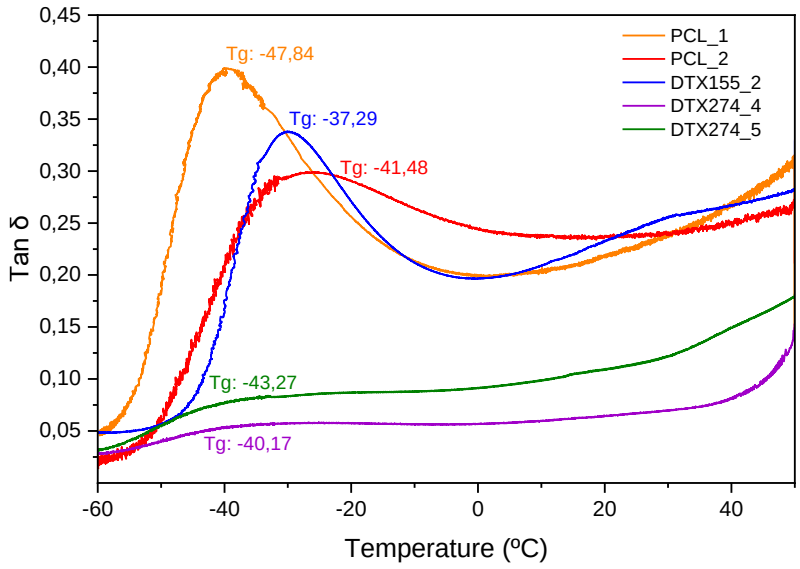

Figure 10 – Tan δ curves of polyurethane films in the temperature range from −60 °C to 50 °C, indicating the glass transition behaviour of the materials.

The PCL-based samples exhibited lower Tg values, confirming the greater flexibility of the soft segments derived from polycaprolactone. The DTX155 formulation showed an intermediate Tg, while the DTX274 series exhibited slightly higher Tg values, indicating greater restriction of segmental motion. This shift towards higher temperatures suggests stronger intermolecular interactions and more pronounced microphase separation between the soft and hard domains [32,57].

Table 13 summarises the glass transition temperatures (Tg) determined from the tan δ peak maximum, the storage modulus (E′) in the glassy state, and E′ in the rubbery plateau region for all formulations.

Table 13 – DMA thermomechanical parameters: glass transition temperature (Tg) from the tan δ peak maximum, storage modulus (E′) in the glassy state and in the rubbery plateau region.

Sample	**T_g (°C)**	**E' (MPa)**	**E" (MPa)**	**E' (MPa)**	**E" (MPa)**
		-60°C		**25°C**	
PCL_1	-41.48	1843.24	82.95	12.34	2.78
PCL_2	-47.84	2492.40	74.54	23.07	5.49
DTX155_2	-37.29	2486.93	122.20	24.03	5.87
DTX274_4	-40.17	2264.79	63.81	738.00	49.47
DTX274_5	-43.27	2133.35	68.58	409.79	47.22

Although all Tg values remain in the negative temperature range, indicating a predominantly amorphous, soft phase with significant molecular mobility, this behaviour remains consistent with the expected structural organization of segmented polyurethanes and can be associated with stronger intermolecular interactions [32,57]. The amorphous nature of the soft domains directly affects melting behaviour, as the degree of chain mobility and phase separation influences crystalline organization and consequently the material's melting temperature [3,57].

The shape and intensity of the tan δ peaks can also provide insight into the structural organization of materials. Broader peaks indicate a wider distribution of relaxation times, which is typically associated with heterogeneous phase morphology. In contrast, sharper peaks suggest a more defined transition and more homogeneous microphase separation. The DTX274 samples exhibited broader, slightly shifted transitions, potentially due to enhanced hydrogen-bonding interactions within the polymer network and variations in chain-extender content [60].

Figure 11 presents the temperature dependence of the storage modulus (E′) and loss modulus (E″) for all formulations. E′ reflects the material's elastic response, representing its stiffness and ability to store mechanical energy. At low temperatures, all

samples exhibited high E′ values, corresponding to the glassy state. As the temperature increased and the materials approached Tg, a significant drop in E′ was observed, marking the transition from the glassy to the rubbery state [60].

Meanwhile, E″, which indicates the viscous component and energy dissipation through molecular motion, exhibited a peak near the glass transition region. This behaviour is characteristic of segmented polyurethanes and reflects the activation of cooperative molecular motions within the soft segments. Above Tg, the materials entered the rubbery plateau region, where E′ stabilized at lower values and mechanical behaviour was dominated by the elastic network formed by the hard segments. The extent of this plateau is directly related to crosslink density and phase organization [60].

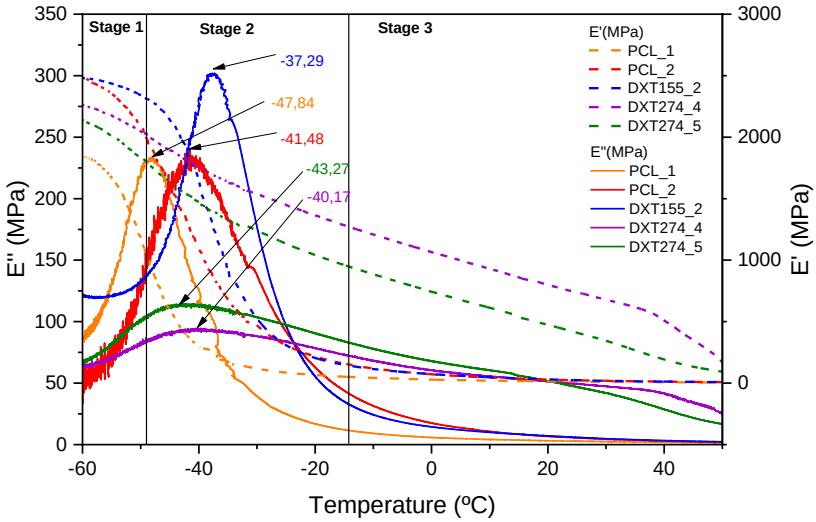

Figure 11 – Storage modulus (E′) and loss modulus (E″) of polyurethane films as a function of temperature, obtained by dynamic mechanical analysis (DMA).

The DTX274_4 and DTX274_5 samples visually appeared more rigid and brittle and maintained comparatively higher modulus values in the rubbery region, indicating a stiffer network structure. In contrast, the PCL-based films and the DTX155 sample exhibited a more pronounced decrease in modulus, consistent with their more flexible and ductile behaviour.

Following thermomechanical characterization, the adhesive performance of the polyurethane dispersions was evaluated using T-peel testing. The results are presented in Figure 12, which shows that PCL_2 exhibited the highest peel force of all the samples. This indicates superior adhesion performance under the test conditions, suggesting that it is suitable for applications requiring effective energy dissipation and cohesive strength, such as footwear bonding.

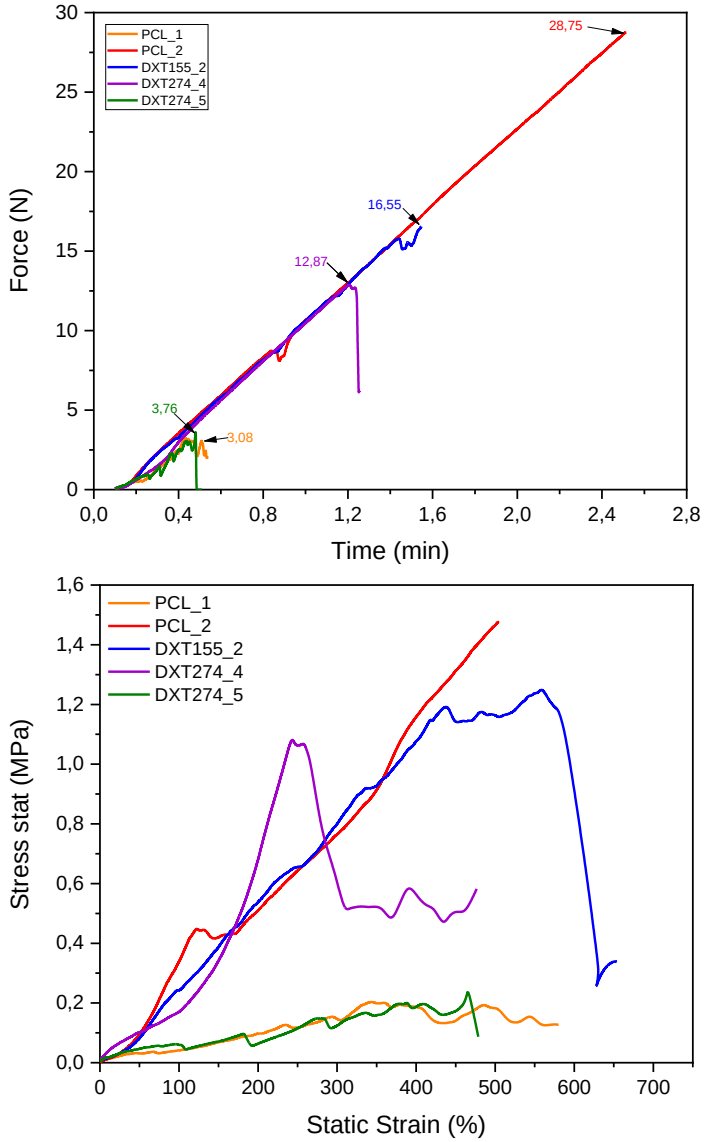

Figure 12 – Adhesive performance evaluated by T-peel test: (a) maximum peel force and elongation at break and (b) representative tensile performance curves.

In contrast, PCL_1 and DTX274_5 demonstrated very low peel resistance, failing at forces below 4 N. The reduced performance of PCL_1 may be associated with its lower cohesive strength and reduced resistance to crack propagation during peeling. For DTX274_5, the poor adhesion behaviour appears strongly related to its rigidity and brittleness, as evidenced by the previous DMA analysis. Excessive stiffness limits molecular mobility and reduces the material's ability to dissipate mechanical energy during debonding. Recent studies report that optimal peel performance requires a balance between elasticity and viscous dissipation: overly rigid systems tend to fail in a brittle manner, resulting in lower peel strength due to limited stress redistribution at the adhesive interface [61].

Both formulations, DTX155_2 and DTX274_4, exhibited intermediate adhesion behaviour. This is consistent with their viscoelastic profiles obtained by DMA, which show a balance between stiffness and segmental mobility, as evidenced by a moderate storage modulus and well-defined tan δ peaks. Polyurethane adhesives with controlled microphase separation and a moderate hard-segment content tend to exhibit improved peel resistance because they combine sufficient cohesive strength with the capacity for plastic deformation during crack propagation [61].

However, it is also important to consider the influence of synthesis conditions. The DTX274 series was prepared at different reaction temperatures (80 °C and 90 °C), which may have altered the extent of phase separation and hard segment organization. The sample synthesized at the higher temperature (DTX274_5) exhibited increased rigidity and reduced peel strength. This is consistent with its higher E′ and reduced tan δ, indicating a stiffer, less energy-dissipative structure during crack propagation. This suggests that higher synthesis temperatures may promote greater structural ordering, potentially at the expense of adhesive performance.

4.6.2 COATINGS

For coating applications, the performance of the films was evaluated in terms of Water vapour permeability (WVP), in accordance with ASTM E96–95 using the cup method under controlled conditions [47]. This test is particularly relevant for materials intended for use in footwear, since water vapour transmission directly affects breathability and thermal comfort. Adequate permeability enables moisture generated by perspiration to diffuse through the material, thereby reducing internal humidity and enhancing user comfort [62]. The WVP values obtained for the developed films are presented in Table 14.

Table 14 – WVP results of polyurethane films, indicating barrier performance.

Sample	**WVP (10^{-12} g / h · mm · Pa)**
PCL_1	4.02 ± 1.27 E-12
PCL_2	6.89 ± 3.77 E-12
DTX155_2	8.25 ± 2.24 E-12
DTX274_4	11.2 ± 3.89 E-12
DTX274_5	18.2 ± 4.66 E-12

Values are expressed as ± mean standard deviation.

In the context of footwear coatings, higher WVP values indicate greater vapour permeability, which improves breathability. More permeable coatings allow perspiration to evaporate more efficiently, reducing moisture accumulation inside the shoe and enhancing the user's thermal comfort.

Of the analysed samples, DTX274_5 had one of the highest WVP values, indicating greater mass loss during the test and, consequently, higher vapour transmission. This suggests that this formulation allows water vapour to diffuse more efficiently through the polymer matrix. DTX274_4 presented WVP values very close to those of DTX155_2, revealing that these two dispersions exhibit similar permeability behaviour.

It is important to note that the difference between the syntheses of DTX274_4 and DTX274_5 lies in the initial reaction temperature. Increasing the temperature at the beginning of the reaction from 80 °C to 90 °C likely influenced the organisation of the polymer chains, their mobility, or the microstructural arrangement, ultimately affecting the diffusion pathways of water vapour. The results suggest that this adjustment caused DTX274_4 to exhibit permeability behaviour comparable to that of DTX155_2, indicating that reaction temperature plays a significant role in tailoring transport properties.

As shown in Figure 13, when the systems are compared globally, the dispersions synthesised from bio-based polyols exhibit superior vapour permeability to the synthetic PCL-based dispersions. Both PCL_1 and PCL_2 exhibited lower WVP values, indicating more restricted vapour diffusion. In practical terms, this suggests that bio-based formulations may offer better breathability in footwear coatings, potentially providing greater comfort without compromising film integrity.

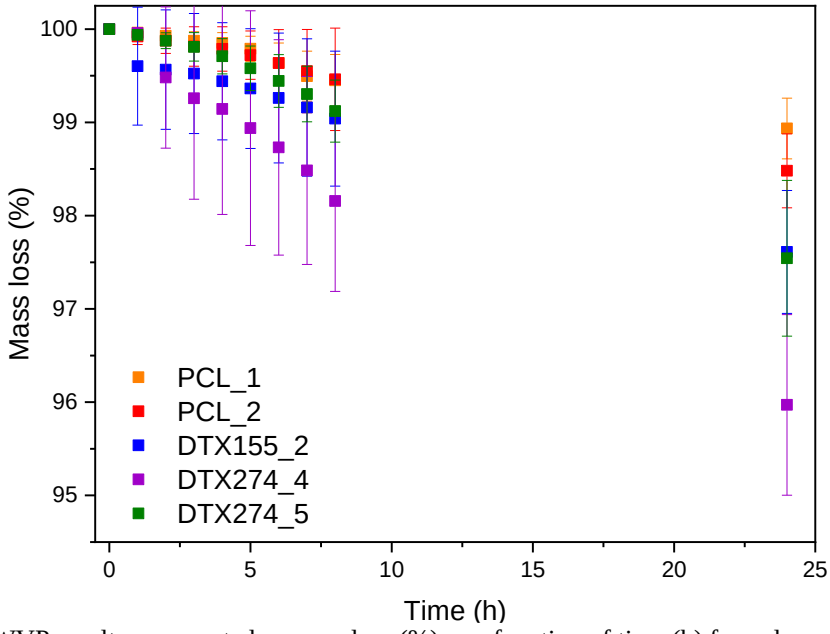

Figure 13 –WVP results represented as mass loss (%) as a function of time (h) for polyurethane films.

Overall, these findings reinforce the idea that formulation parameters — particularly the type of polyol and reaction conditions — strongly influence vapour transport properties, enabling the design of coatings with optimised breathability for end-use applications.

4.6.3 AGGLOMERATES

Duplicate plates were produced for the cork composite application using each dispersion as a binder. All of the resulting composites had a similar appearance and colour, and formed compact, homogeneous structures after pressing, Figure 14. During preparation, slight differences in moisture distribution and wettability were observed, depending on the dispersion used; some formulations interacted more readily with the cork particles during mixing. However, after pressing, the resulting composites showed no visible differences in compactness or overall uniformity, regardless of the formulation applied.

The water adsorption and desorption capacity of the composite samples was evaluated in accordance with ISO 22649:2016. According to this standard, adequate performance is achieved when water absorption (Wa) exceeds 70 mg/cm² and water desorption (Wd) is at least 60%. Table shows the results of the samples in Table 15.

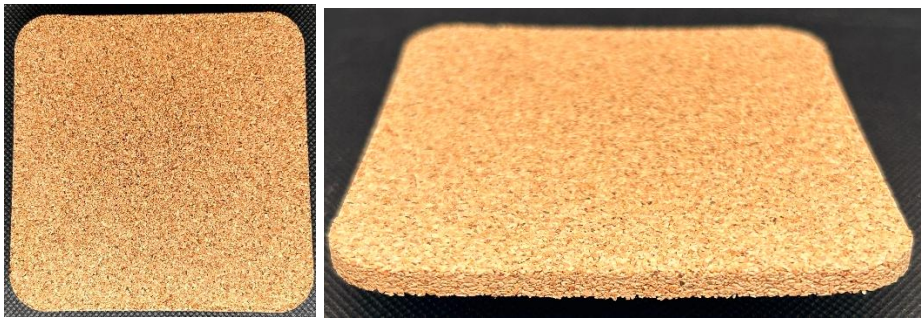

Figure 14 –Cork composite sample produced using aqueous polyurethane dispersions.

Table 15 – Water absorption and desorption capacity of cork-based composites

Sample	Wa (mg/cm²)	Wd (%)
PCL_1	99.43 ± 7.95E+00	89.39 ± 2.27E+00
PCL_2	61.34 ± 3.46E+00	94.28 ± 1.74E-01
DTX155_2	93.17 ± 0.60E+00	85.07 ± 6.01E-01
DTX274_4	65.31 ± 3.54E+00	96.76 ± 1.09E-01
DTX274_5	54.00 ± 3.04E+00	97.11 ± 2.67E-01

Values are expressed as ± mean standard deviation.

Water absorption is essential because it removes moisture from the foot's surface, ensuring the end user's comfort while wearing the shoes. In turn, water desorption directly affects the drying rate after use, thereby contributing to hygiene and overall wearing comfort. Therefore, both parameters must be considered together in order to properly assess the material's functional performance [62,63].

Of the analysed samples, PCL_1 (99.43 mg/cm²; 89.39%) and DTX155_2 (93.17 mg/cm²; 85.07%) met both normative criteria. This behaviour indicates balanced moisture management performance, as these materials can absorb sufficient water during use and release it efficiently during drying. This equilibrium is particularly desirable in footwear applications, where sweat uptake and drying capacity are critical.

However, PCL_2 (61.34 mg/cm²; 94.28%), DTX274_4 (65.31 mg/cm²; 96.76%), and DTX274_5 (54.00 mg/cm²; 97.11%) failed to meet the minimum absorption requirement despite demonstrating excellent desorption performance. The high desorption percentages observed should be interpreted with caution since the initial absorbed water content was below the minimum threshold established by the standard. Therefore, the elevated Wd values likely reflect the release of a relatively small amount of absorbed water, rather than superior moisture management capability. In practical terms, while these materials dry quickly, their limited absorption capacity may reduce their effectiveness at removing moisture from the foot surface during use, which could compromise comfort under real conditions.

It was also observed that the synthetic materials (PCL_1 and PCL_2) exhibited different behaviours, indicating that small variations in formulation can significantly influence the balance between absorption and desorption. In contrast, DTX155_2 performed similarly to PCL_1, meeting both normative criteria simultaneously. This suggests that DTX155_2 could be a promising bio-based alternative to synthetic systems for agglomerating cork insoles in industrial applications requiring efficient moisture management and user comfort.

5 CONCLUSION AND FUTURE WORKS

The aim of this work was to develop and characterise aqueous polyurethane dispersions based on bio-based polyols and to compare their performance with dispersions derived from synthetic polyols for different footwear industrial applications.

The synthesized dispersions exhibited pH values near neutrality (≈7.4–7.7), indicating effective neutralization and adequate electrostatic stabilization. Most formulations showed solids content within the typical range for stable PUDs, between 32% and 40%, while the viscosity values reflected the degree of chain extension and intermolecular interactions. In this context, the biobased systems DTX155_2, DTX274_4, and DTX274_5 exhibited rheological and colloidal behaviour comparable to the synthetic references PCL_1 and PCL_2, confirming the feasibility of producing stable dispersions from renewable raw materials. The zeta potential of these samples DTX155_2 (−47.94 mV), DTX274_4 (−48.63 mV), and DTX274_5 (−48.38 mV) pointed to stable dispersions.

The PCL-based systems exhibited smaller particle sizes due to their greater hydrophilicity, whereas the DTX-based dispersions showed slightly larger particles, attributable to the greater hydrophobic contribution of the biobased polyols. Nevertheless, the stability in the presence of electrolyte confirmed the adequate distribution of ionic groups along the polymer chains.

In adsorption/desorption tests, DTX155_2 showed excellent performance (93.17 $mg \cdot cm^{-2}$ and 85.07%), comparable to the commercial reference PCL_1 (99.43 $mg \cdot cm^{-2}$ and 89.39%) in terms of balanced behaviour, simultaneously meeting the two regulatory requirements. Therefore, it can be considered an excellent substitute for the material currently used in industry. In contrast, PCL_2, DTX274_4, and DTX274_5 did not reach the minimum absorption requirement, although all of them presented desorption values above 94%, indicating efficient moisture release. This behaviour is directly reflected in

the water vapour permeability results, where the highest WVP values were obtained for DTX274_4 (11.2×10^{-12} $g \cdot m^{-1} \cdot s^{-1} \cdot Pa^{-1}$) and DTX274_5 ($18.2 \times 10^{-12}$ $g \cdot m^{-1} \cdot s^{-1} \cdot Pa^{-1}$), followed by DTX155_2, all significantly higher than PCL_1 (4.02×10^{-12}) and PCL_2 (6.89×10^{-12}). This demonstrates that DTX274_4 and DTX274_5 are better suited for breathable coating applications, while DTX155_2 stands out as the most promising bio-based alternative for agglomerated cork systems due to its moisture-adsorption capacity.

The peel strength results showed that the DTX-based dispersions still have limitations for adhesive applications, with maximum values of 16.55 N for DTX155_2, 12.87 N for DTX274_4 and only 3.76 N for DTX274_5, comparable to PCL_1 and significantly lower than PCL_2 (28.75 N). This behaviour is directly related to the mechanical character of the films. The PCL-based films and DTX155_2 were more flexible and malleable due to their lower glass transition temperatures and greater soft-segment mobility, thereby favouring energy dissipation during peeling. In contrast, the DTX274-based films were more rigid and opaque, indicating a more restricted segmental motion and a stiffer polymeric network, which contributes to higher vapour permeability but reduces adhesive performance.

Overall, the results demonstrate that biobased polyols are a viable option for producing stable aqueous polyurethane dispersions with properties comparable to those of synthetic systems, and they clearly have potential for industrial application. DTX155_2 is the most promising formulation to be used as cork agglomerates due to its adsorption/desorption ability, surpassing even the conventional PCL_1 in terms of balanced performance. Meanwhile, DTX274_4 and DTX274_5 stand out as breathable coating materials due to their high electrolyte stability and superior water vapour permeability.

Future work may involve using mixtures of biobased and synthetic polyols to balance flexibility and rigidity, depending on the intended application, such as improving adhesive performance or enhancing permeability. Additionally, adjusting the chain extender content could promote higher long-term dispersion stability. Finally, alternative adhesive testing methodologies that more closely reflect the conditions under which these systems are used in the footwear industry should be investigated to enable a more accurate assessment of their performance.

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7 APPENDIX

7.1 APPENDIX A

Table A1 – Process parameters and synthesis data of the aqueous polyurethane dispersions, including conversion, solvent content, and reaction conditions.

			First Stage	Second Stage	Third Stage					
Sample	**Water (mL)**	**Acetone (mL)**	**Theorical conversion (%)**	**Experimental Conversion (%)**	**Theorical conversion (%)**	**Experimental Conversion (%)**	**Experimental Conversion (%)**	**Final Biobased content (%)**	**Chain extension (%)**	**Status**
PCL_1	120	20	28.65	34.64	59.88	77.42	87.70	-	60	Stable
PCL_2	120	25	33.59	37.40	59.9	72.46	82.05	-	60	Stable
DTX155_1	120	25	28.66	25.76	59.93	67.79	89.65	68.48	60	No Stable
DTX155_2	170	60	28.65	12.55	59.86	71.28	71.81	68.47	40	Stable
DTX274_1	120	25	28.76	21.47	59.98	56.48	94.59	68.71	60	No Stable
DTX274_2	120	100	28.67	32.81	58.89	75.06	89.35	-	60	No Stable
DTX274_3	170	125	28.69	16.70	59.91	54.00	50.69	68.50	60	No Stable
DTX274_4	170	75	28.65	15.40	59.88	68.95	77.98	68.47	40	Stable
DTX274_5	170	100	28.65	14.94	59.87	62.24	69.42	68.47	40	Stable

Figure A1 – Visual appearance of the DTX274_2 dispersion showing phase destabilization and gel formation after synthesis.

7.2 APPENDIX B

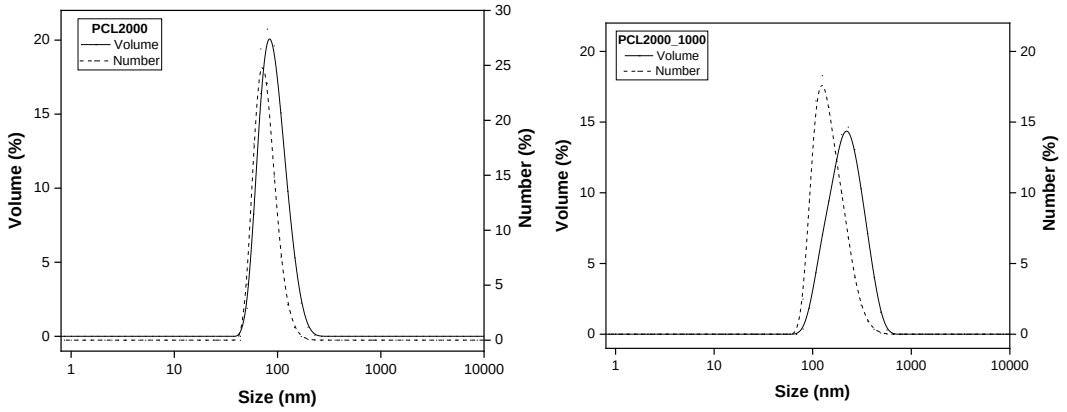

Figure B1 – Particle size distribution of PCL-based dispersions represented by volume and number.

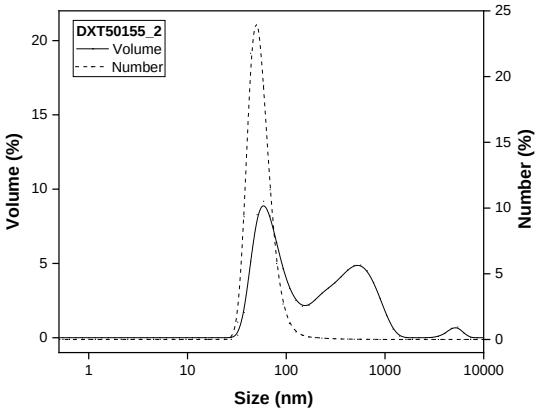

Figure B2 – Particle size distribution of DTX155_2 dispersion represented by volume and number.

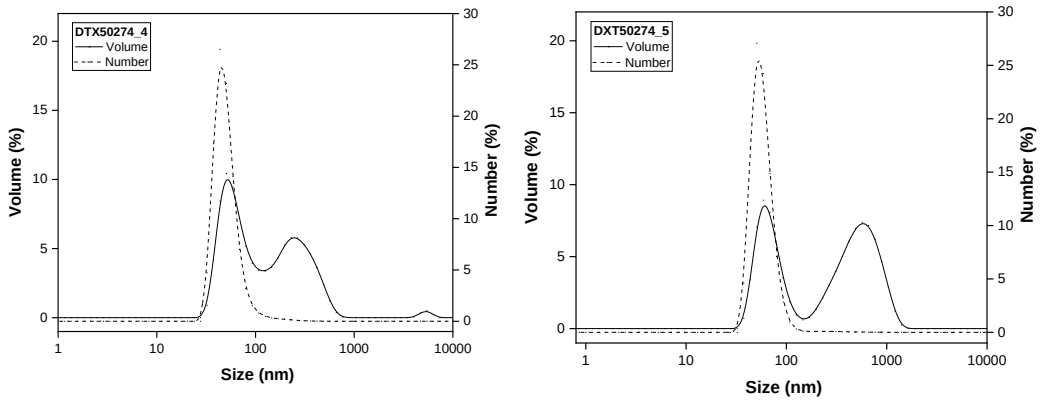

Figure B3 – Particle size distribution of DTX274-based dispersions represented by volume and number.

7.3 APPENDIX C

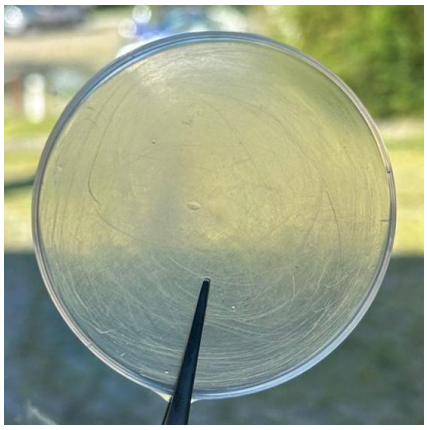

Figure C1 –Film obtained from PCL_2 dispersion after drying under ambient conditions.

Figure C2 – Film obtained from DTX274_4 dispersion after drying under ambient conditions.

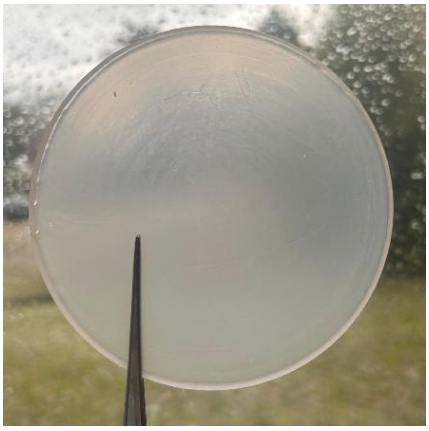

Figure C3 – Film obtained from DTX274_5 dispersion after drying under ambient conditions.

7.4 APPENDIX D

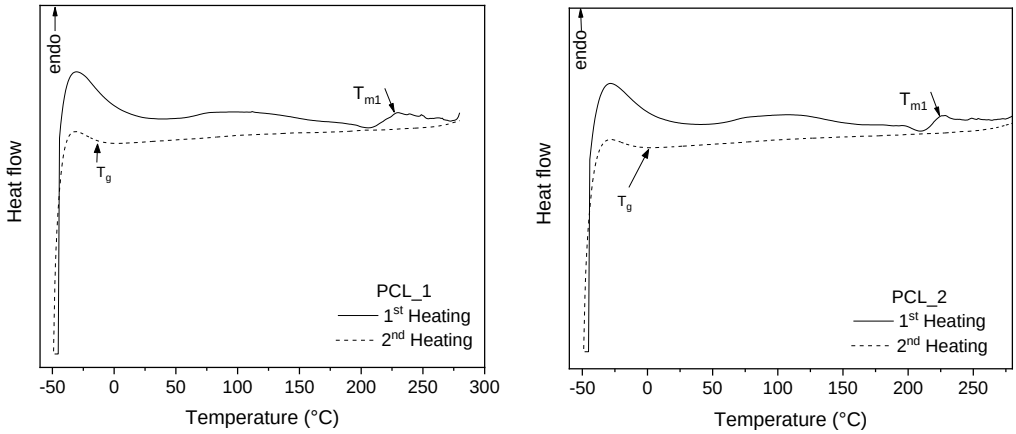

Figure D1 – DSC curve of PCL-based polyurethane films.

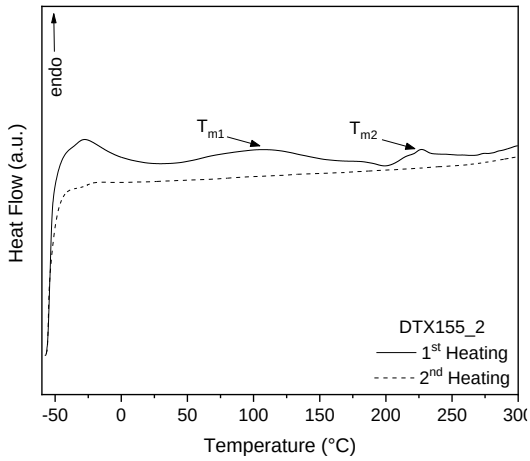

Figure D2 – DSC curve of DTX155-based polyurethane films.

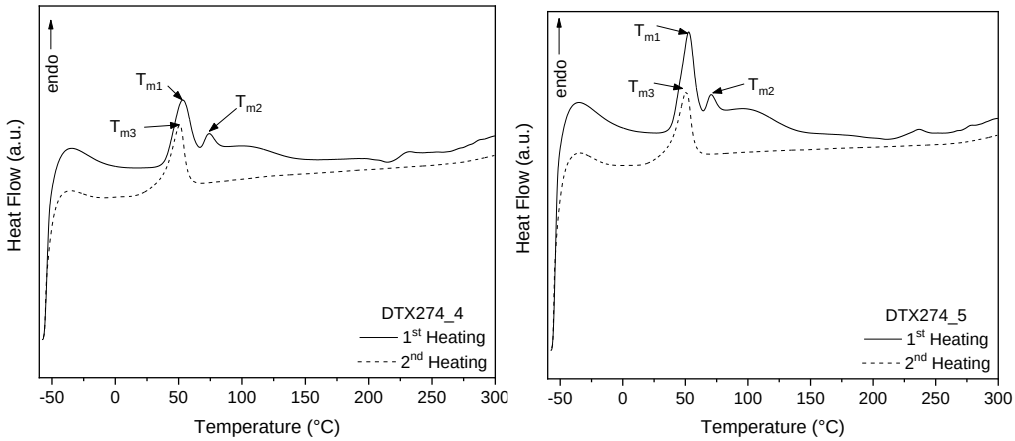

Figure D3 – DSC curve of DTX274-based polyurethane films.

7.5 APPENDIX E

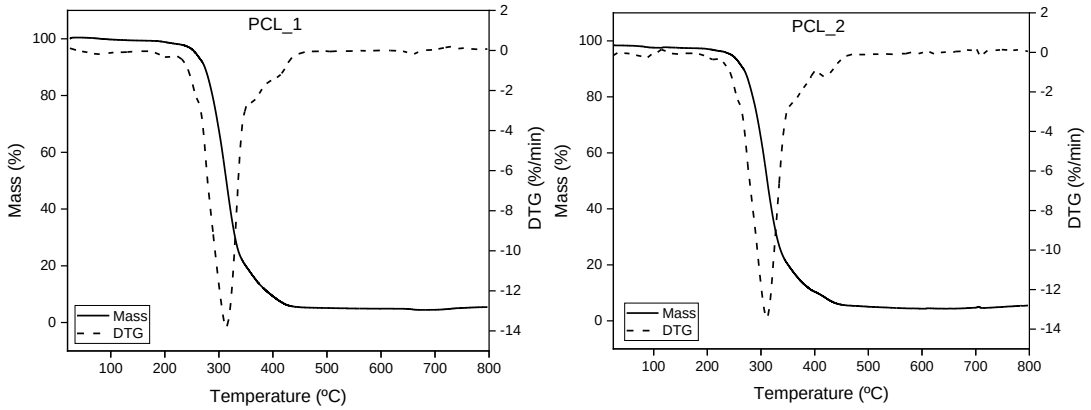

Figure E1 – TGA curve of PCL-based polyurethane films.

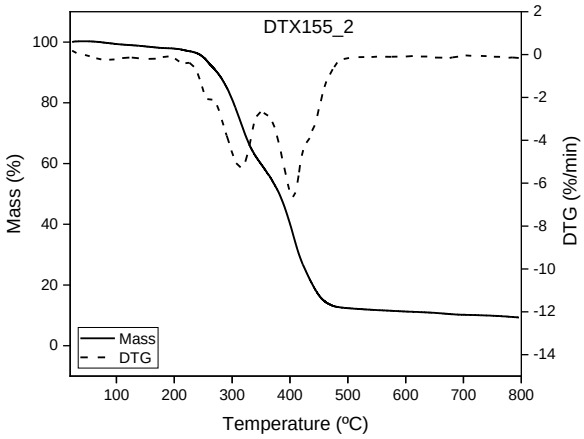

Figure E2 – TGA curve of DTX155-based polyurethane films.

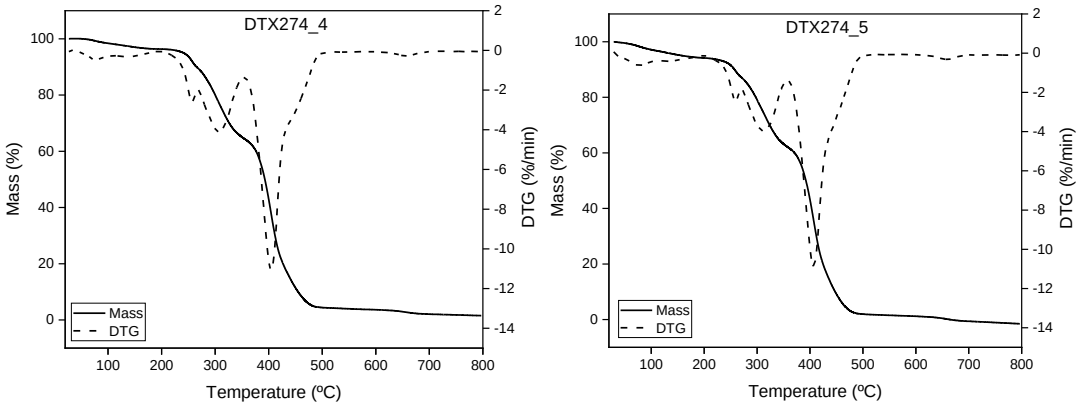

Figure E3 – TGA curve of DTX274-based polyurethane films.