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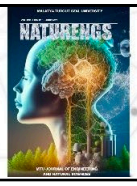

Research Article

Synthesis and Characterization of Cellulose Based Injectable Polyurethane Gels

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ABSTRACT

This article describes the synthesis and characterization of cellulose-based injectable polyurethane gels for tissue engineering applications. The gels were prepared by combining a cellulose derivative with a polyurethane precursor and crosslinking agent to form a stable gel under physiological conditions. The resulting gels were evaluated for their swelling behavior. The addition of cellulose to polyurethane is a promising approach to improve the properties of polyurethane. Cellulose, is an abundant, environmentally friendly, and inexpensive polysaccharide polymer widely used in hydrogels, pharmaceuticals, and agriculture. The cellulose-based polyurethane composites obtained in this study were extensively characterized using various techniques such as Fourier transform infrared spectroscopy (FT-IR), Thermogravimetric Analyzer (TGA), Differential Scanning Calorimeter (DSC), Differential Thermal Analysis (DTA), swelling test measurements and optical microscopy. The results demonstrated that the obtained composites are suitable for the production of injectable insulating materials. The paper also briefly discusses the various uses of polyurethanes in different fields, including furniture manufacturing, medical devices (e.g., hospital beds, catheters, injection-coated devices, wound dressings, and surgical dressings), as well as marine, air, and land vehicles. In conclusion, this paper provides valuable insights into the development of cellulose-based injectable polyurethane gels for tissue engineering applications and highlights the potential of cellulose as an additive to enhance the properties of polyurethane. The results of this study may contribute to the development of new and improved biomaterials for tissue engineering applications.

Keywords**:** *Polyurethanes, Cellulose, Injectable, Gels.*

Introduction

Cellulose is a polysaccharide consisting of glucose monomers linked by β-1,4 glycosidic bonds. It is the most abundant natural polymer and an essential component of plant cell walls. Cellulose is classified as a linear homopolymer and a biopolymer. Due to its abundant availability, biocompatibility, and biodegradability, cellulose has gained attention in various applications, including biomedical, food, and paper industries [1]. Cellulose can be classified based on its sources, which include wood pulp, cotton, and agricultural waste [2]. Wood pulp-based cellulose is mainly used in the paper and pulp industry, while cotton-based cellulose finds application in the textile industry. Agricultural waste-based cellulose, such as rice straw, wheat straw, and corn husk, has gained attention as a sustainable and renewable source for the production of cellulose-based materials [3]. In terms of its structural and morphological features, cellulose can be classified as crystalline and amorphous. The crystalline region consists of highly ordered and tightly packed cellulose chains, while the amorphous region consists of randomly arranged cellulose chains. The degree of crystallinity of cellulose varies depending on the source and the method of preparation [4].

Polyurethane is a versatile polymer known for its exceptional mechanical properties, chemical resistance, and thermal stability [5]. It is synthesized through the reaction of diisocyanates with polyols, resulting in a polymer with urethane linkages (-NHCOO-) in its backbone [6]. Polyurethane materials can be classified into thermoplastic polyurethanes (TPUs) and thermosetting polyurethanes (TSPUs) based on their structure [7]. TPUs are linear polymers that can be melted and remolded, while TSPUs are crosslinked polymers that cannot be remolded [7]. The unique properties of polyurethane make it suitable for a wide range of applications. In the automotive industry, polyurethane is extensively used for manufacturing car seats, dashboards, and other interior parts due to its durability and comfort [8]. It finds application in the construction industry as insulation, adhesives, coatings, and sealants, offering excellent thermal and moisture

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resistance [5]. In the electronics industry, polyurethane is utilized for potting compounds, encapsulants, and adhesives to protect sensitive electronic components [6]. The textile industry benefits from polyurethane in the production of synthetic leather, coatings, and adhesives due to its flexibility and abrasion resistance [7]. Additionally, polyurethane finds widespread use in the medical field for manufacturing catheters, implants, wound dressings, and drug delivery systems owing to its biocompatibility and versatility [8].

Polyurethane materials exhibit several advantages, such as high durability, flexibility, and resistance to chemicals, oils, and solvents [5]. However, they also have limitations, including flammability and the emission of harmful gases when burned [5].

The synthesis of polyurethanes can be achieved by different methods, including one-shot, prepolymer, and quasi-prepolymer methods [9]. In the one-shot method, all the reactants, including the polyol, diisocyanate, and any chain extenders or catalysts, are mixed together and reacted simultaneously. In the prepolymer method, a diisocyanate is reacted with a polyol to form an isocyanate-terminated prepolymer, which is then reacted with a chain extender to form the final polyurethane. In the quasi-prepolymer method, a portion of the polyol is reacted with a diisocyanate to form a prepolymer, which is then mixed with the remaining polyol and chain extender to form the final polyurethane.

Various types of polyols, diisocyanates, and chain extenders can be used in the synthesis of polyurethanes, depending on the desired properties of the final polymer. For example, polyether polyols are often used to produce flexible polyurethane foams, while polyester polyols are used to produce rigid polyurethane foams [10]. Polyurethane gels have attracted significant attention in recent years due to their excellent mechanical properties, biocompatibility, and biodegradability. The injectable polyurethane gels have potential applications in tissue engineering, drug delivery, and wound healing due to their ability to conform to the shape of the wound and to be easily injected. In this study, we present the synthesis and characterization of cellulose-based injectable polyurethane gels.

Material and Methods

Chemicals and Equipment

The mentioned cellulosic materials were commercially available. Polyethylene glycol-1000 (PEG-1000), dimethylformamide (DMF), hexamethylene diisocyanate (HMDI) and dibutyltin dilaurate (DBTL) were obtained from Sigma-Aldrich.

The characterization of cellulose-based polyurethane gels' structure was determined utilizing the FT-IR spectroscopy method. The FT-IR analysis was conducted using the Perkin Elmer Spectrum 2 model FT-IR spectrophotometer. The analysis was performed in the attenuated total reflection (ATR) mode, and the recorded spectra covered a range of 400-4000 cm-1.

To examine the thermal properties of the cellulose-based polyurethane gels, DTA, DSC, and TGA devices were employed. DTA measurements were carried out to assess the thermal strength of the gel structure's scope for this study. The Shimadzu DTA-50 instrument was used to determine the thermal stability of the gel structures. The analysis was conducted with respect to an aluminum oxide reference material at a heating rate of 10 mg sample per 10 °C/min. The softening temperatures and glass transition temperature (Tg) of the polymeric gel structures were measured utilizing the Shimadzu DSC-60 model calorimeter. These analyses employed a heating rate of 5 °C/min and a 5 mg sample. The samples under investigation were placed in aluminum pans with alpha alumina reference material in a static air atmosphere, covering a temperature range of 30-500 °C. TGA analysis was performed using the Shimadzu TGA 60 instrument. TGA thermograms were recorded at a heating rate of 10 °C/min, utilizing a sample weighing 10 mg, in a static air atmosphere.

Synthesis of Polyurethanes

In the process of synthesizing polyurethane, a solution was prepared by dissolving 1 gram of PEG-1000 in 3 milliliters of dimethylformamide (DMF) within a three-necked flask. Simultaneously, in a separate tube, a solution was prepared by combining 0.168 milliliters of hexamethylene diisocyanate (HMDI) with 2 milliliters of DMF. This tube solution, containing HMDI, was then slowly added dropwise to the PEG-1000 solution within the three-necked flask, while the mixture was stirred magnetically under a nitrogen atmosphere. As a catalyst, 4 drops of dibutyltin dilaurate (DBTL) were introduced into the mixture. The entire mixture was magnetically stirred at a temperature of 80 ºC for 2 hours, maintaining a nitrogen atmosphere. The progress of polyurethane synthesis was subsequently monitored FT-IR spectroscopy.

Preparation of Cellulose-Based Polyurethane Gels:

To prepare cellulose-based polyurethane gels, commercially available cellulosic materials such as Excelcon, 6158, 4831, and chitin were employed. In this process, 500 microliters of the synthesized polyurethane were combined with 300 microliters of cellulose-based materials (Excelcon, 6158, 4831, and chitin) at a weight concentration of 1%. The resulting mixture was thoroughly blended using a vortex mixer for approximately 1 minute, ensuring a homogeneous composition. Subsequently, the mixture was placed in an oven set at 37 ºC to initiate gelation. Remarkably, gel formation was observed within a rapid time frame of two minutes. Figure 1 was shown the gel formation.

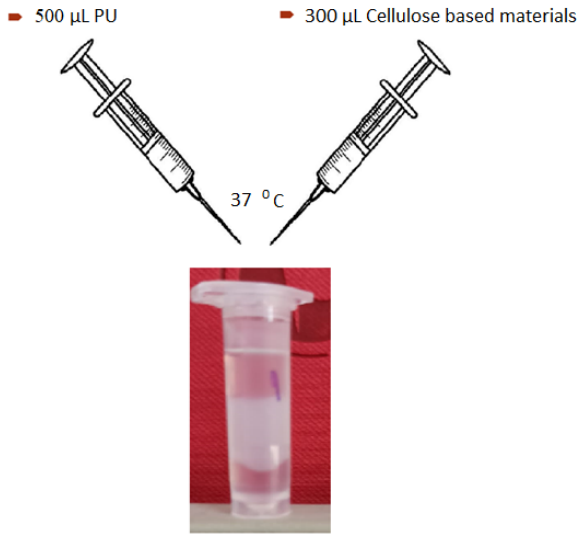

Figure 1. Gel formation of cellulose based-PU

Results and Discussion

The FT-IR spectroscopy technique has been used to analyze the chemical composition of polyurethanes. The FT-IR spectrum provides information on the functional groups present in the polymer, allowing for identification of the urethane bond (N-H and C=O stretching vibrations), the carbonyl group (C=O stretching vibration), and the urea group (C-N stretching vibration) [11]. In Figure 2 and Figure 3 was shown the FT-IR spectrum of commercial cellulosic materials and cellulose based-PU, respectively.

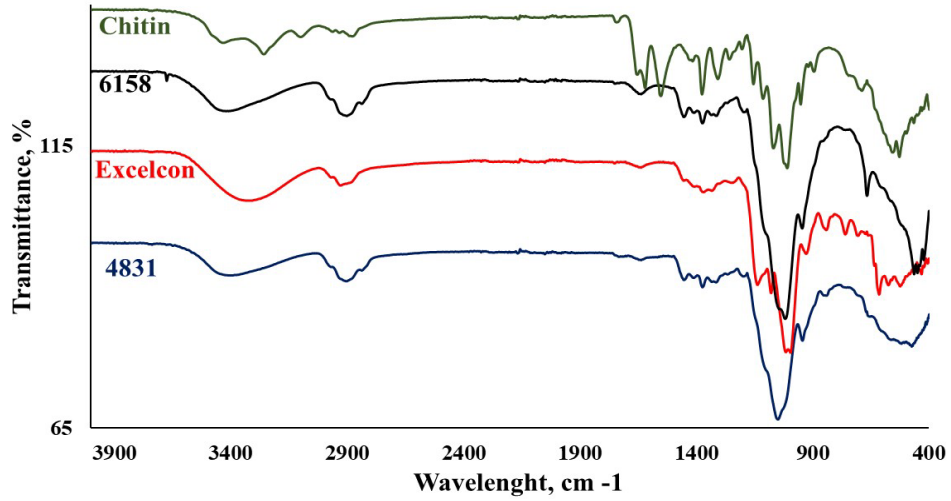

Figure 2. FT-IR spektrum of commercial cellulose materials

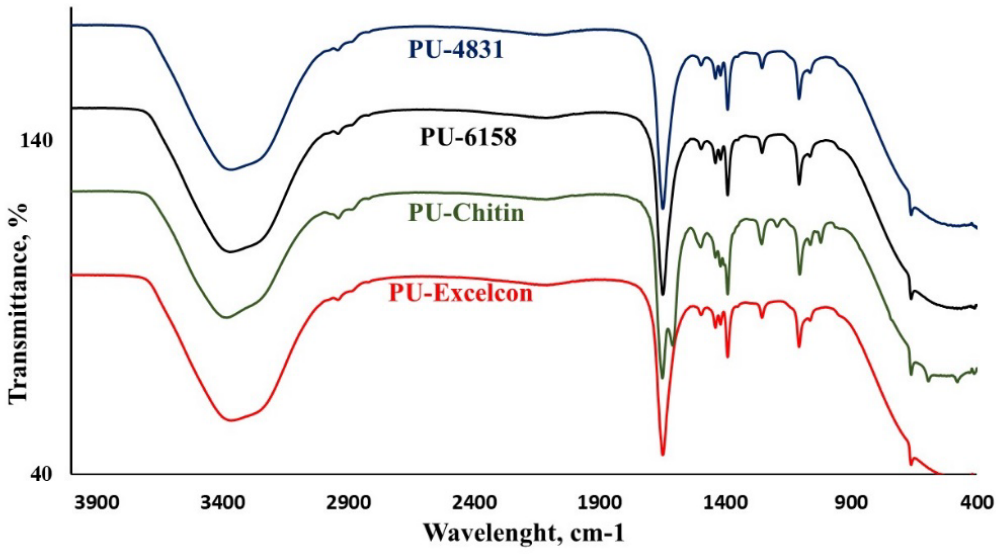

Figure 3. FT-IR spectrum of Cellulose based-PU structures

After the FT-IR spectra and gelation behavior of cellulosic materials were investigated, the thermal properties of commercial 4831 celluloses were investigated by TGA, DTA, and DSC.

Figure 4 was shown cellulose-based-PU TGA's. Thermogravimetric analysis (TGA) is a thermal analysis technique used to determine the thermal stability of polyurethanes. The sample is heated under a controlled atmosphere, and the weight loss is measured as a function of temperature. TGA can provide information on the decomposition temperature, thermal stability, and degradation behavior of the polymer [12,13].

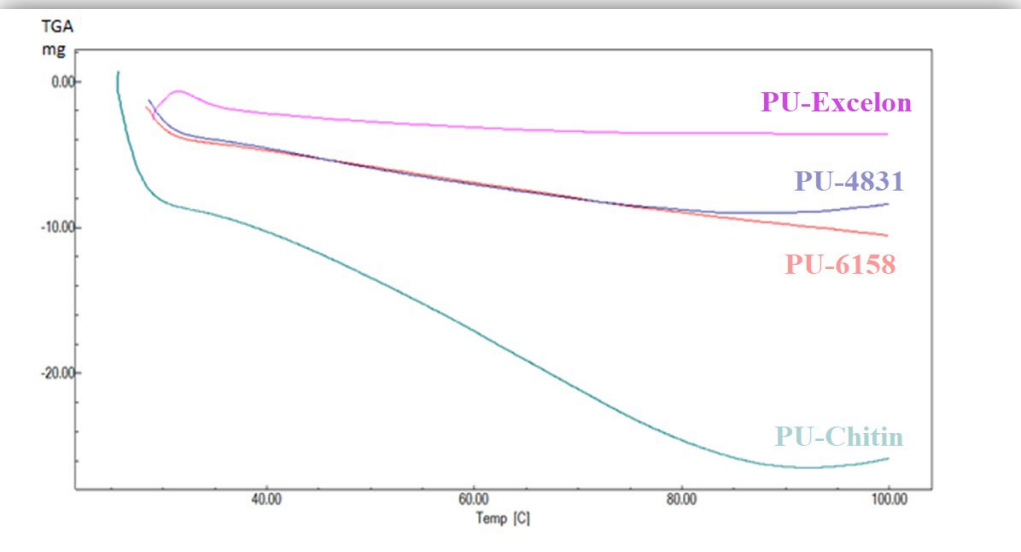

Figure 4. TGA of cellulose-based-PU

Differential thermal analysis (DTA) is another thermal analysis technique used to study the thermal behavior of polyurethanes. The technique measures the temperature difference between a sample and a reference material as they are heated or cooled under a controlled environment. DTA can provide information on the melting temperature, glass transition temperature, and phase transitions of the polymer [14]. Figure 5 was shown the similar behavior of cellulose-based-PUs.

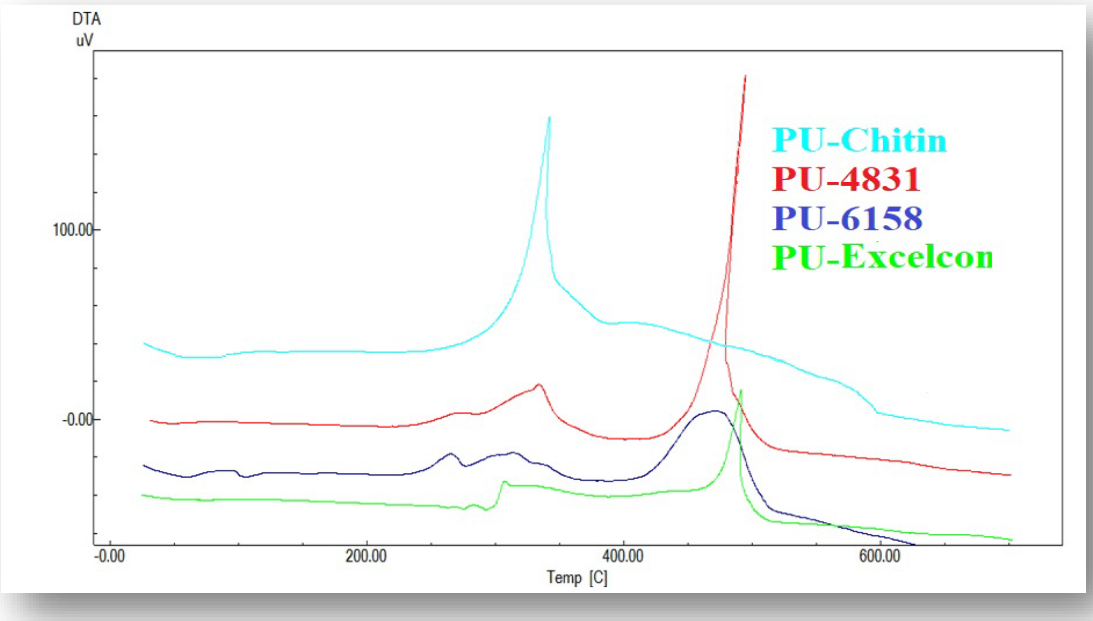

Figure 5. DTA thermogram of cellulose based-PU

Figure 6 demonstrates that chitin was shown differently, but the other cellulose-based-PU responded similarly. And differential scanning calorimetry (DSC) is a technique used to study the thermal behavior of polymers, including polyurethanes. It measures the heat flow as a function of temperature as the sample is heated or cooled under a controlled environment. DSC can provide information on the glass transition temperature, melting temperature, and heat capacity of the polymer [12, 13].

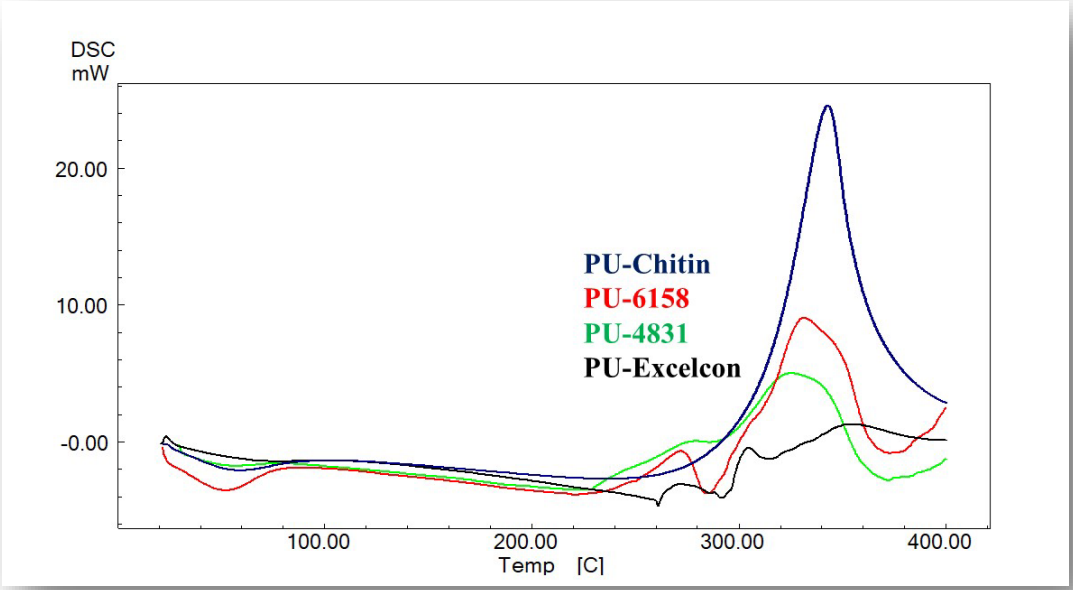

Figure 6. DSC of cellulose-PU gels

Swelling tests for polyurethanes, including injectable polyurethanes, are commonly performed by immersing the samples in a suitable solvent and monitoring the change in weight or volume over time. The degree of swelling can be used to infer the crosslinking density, molecular weight between crosslinks, and other physical and chemical properties of the polymer.

For example, in a study on the synthesis and characterization of injectable polyurethane gels, the authors performed a swelling test by immersing the samples in a phosphate-buffered saline (PBS) solution and measuring the swelling ratio after different time intervals [15]. Similarly, in another study on the synthesis of bio-based polyurethane foams, the authors performed a swelling test by immersing the samples in acetone and measuring the change in weight over time [16]. In Figure 7, it is seen from the optical microscope images that the materials are not similar. at the same time SEM images of Figure 8 support this knowledge.

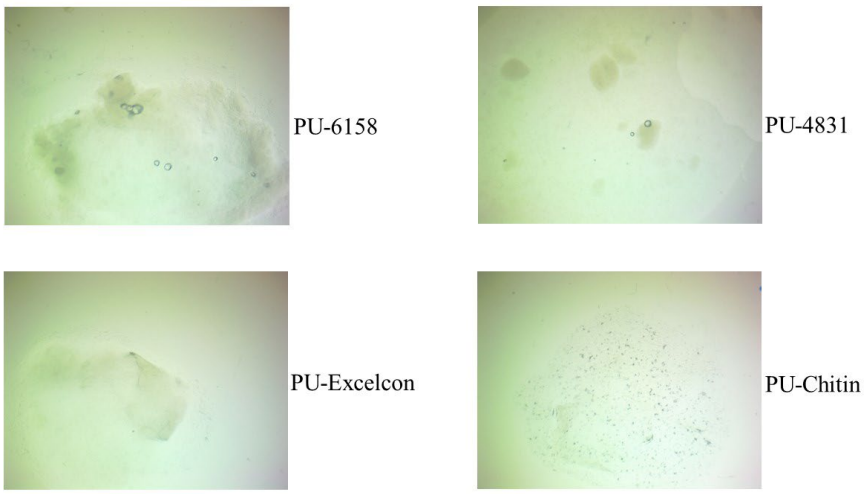

Figure 7. Optic microscope images of cellulose based-PU

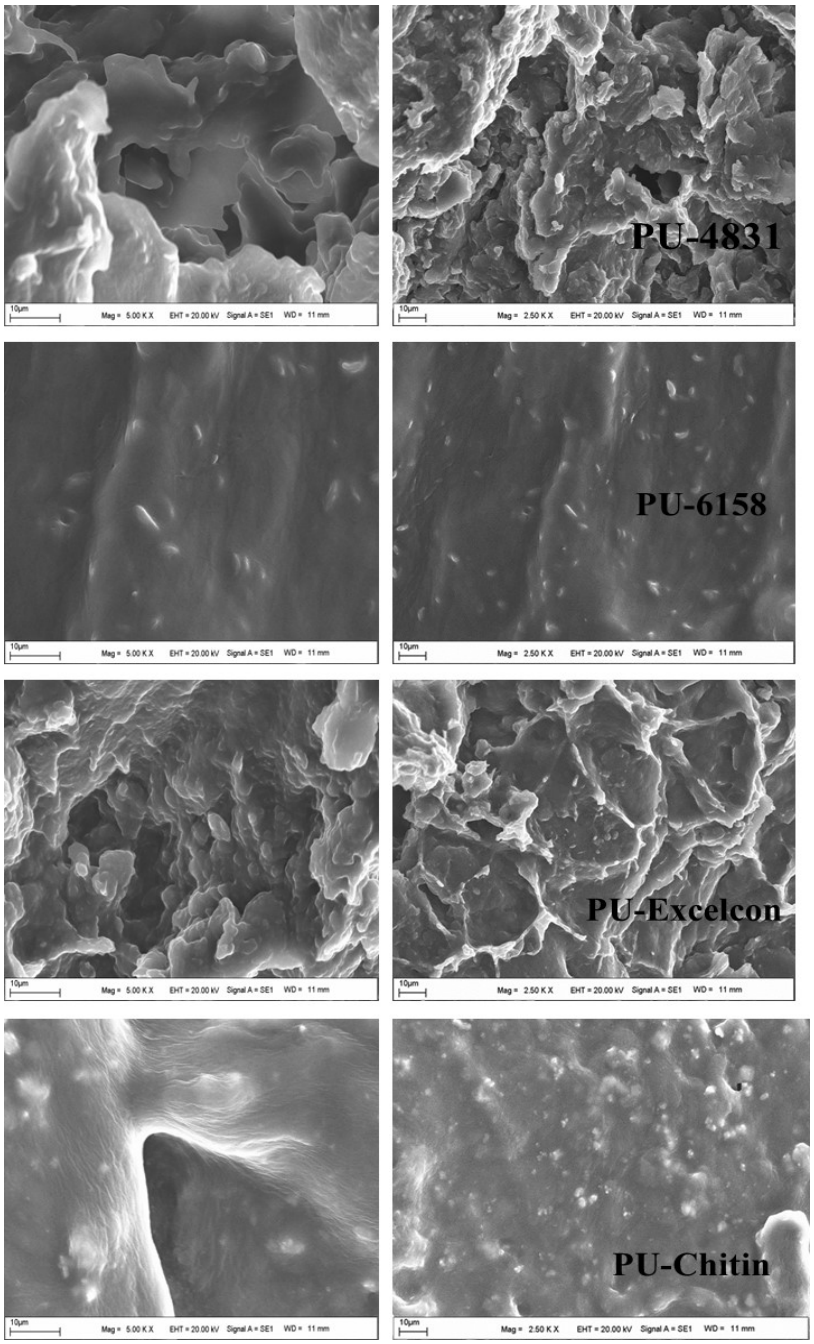

Figure 8. SEM images of cellulose based-PU with different magnification

Swelling test studies were carried out in pH 7 PBS solution, especially since it is similar or compatible with the blood sample. For the swelling test, 1, 1.5, 2 and 3% by mass solutions of cellulosic materials were prepared. The prepared samples were weighed before being placed in PBS solution. To the eperdorfs containing the mentioned samples, 1 mL PBS was added and weighed at regular intervals to determine the swelling rate. Maximum swelling was observed at 60 minutes for samples PU-Excelcon, PU-4831, and PU-Chitin, while maximum swelling was reached at 120 minutes for a sample of PU-6158.

Cellulose-based injectable polyurethane gels have gained attention as a potential biomaterial for tissue engineering and drug delivery applications due to their biocompatibility, biodegradability, and tunable mechanical properties [17]. The synthesis of cellulose-based injectable polyurethane gels typically involves the reaction of a cellulose derivative, such as carboxymethyl cellulose (CMC), with a diisocyanate and a chain extender in the presence of a catalyst [18]. The resulting gel can be injected into a desired site and will set in situ, forming a stable gel network.

One study reported the synthesis of a CMC-based injectable polyurethane gel using hexamethylene diisocyanate and 1,4-butanediol as the chain extender [19]. The resulting gel exhibited a compressive modulus of 3.9 ± 0.7 kPa and showed good injectability and biocompatibility in vitro. Another study reported the synthesis of a CMC-based injectable polyurethane gel

using poly(ethylene glycol) (PEG) as the chain extender [20]. The resulting gel exhibited a compressive modulus of 20-30 kPa and showed good biocompatibility in vitro.

In addition to CMC, other cellulose derivatives, such as hydroxypropyl cellulose (HPC) and methyl cellulose (MC), have also been used in the synthesis of injectable polyurethane gels [21, 22]. The properties of the resulting gels can be tuned by varying the type and amount of cellulose derivative, diisocyanate, and chain extender used.

Overall, cellulose-based injectable polyurethane gels have shown promise as a versatile biomaterial with potential applications in tissue engineering and drug delivery. Further studies are needed to investigate the in vivo biocompatibility and efficacy of these gels.

Conclusions

In conclusion, the synthesis and characterization of cellulose-based injectable polyurethane gels have great potential for new areas and human uses. These materials offer a sustainable and renewable option for biomedical applications, and their improved biocompatibility, biodegradability, and mechanical properties make them an attractive candidate for use in tissue engineering, wound healing, drug delivery, and medical implants.

The development of such materials also aligns with the growing trend of using natural and renewable resources to produce sustainable materials. This approach not only benefits the environment but also helps to address the increasing demand for biocompatible materials in the biomedical field.

Furthermore, the incorporation of nanomaterials and smart functionalities into polyurethane gels can lead to the development of novel applications and technologies. This advancement can contribute to related new areas, such as nanotechnology and smart materials, and help to address various challenges in the biomedical field.

Overall, the synthesis and characterization of cellulose-based injectable polyurethane gels offer exciting opportunities for new areas and human uses, contributing to the development of innovative biomaterials and technologies with potential to improve human health and wellbeing.

Conflict of Interest

No conflict of interest was declared by the authors. F.B.E. and F.N.K contributed equally to this work

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