Energy-Saving Microwave-Assisted Synthesis of PLA for PU/PLA Hybrid Multifunctional Coatings in Drug Release

Vladan Mićić[1, *], Marija Krstic[2], Darko Manjenčić[3], Suzana Cakić[4], Ivan Ristić[2]

[1] *Faculty of Technology Zvornik, University of East Sarajevo, Karakaj 34A, 75400 Zvornik, Republic of Srpska, Bosnia and Herzegovina*

[2] *University of Novi Sad, Faculty of Technology Novi Sad, Boulevard cara Lazara 1, 21101 Novi Sad, Serbia*

[3] *Academy of Kruševac, Department of Technical and Technological Studies, Kosančićeva 36, 37000 Kruševac, Serbia*

[4] *University of Niš, Faculty of Technology, Bulevar oslobođenja 124, 16000 Leskovac, Serbia*

https://doi.org/10.65614/uisk_yucorr.2025.26.ch5

[*]*micicvladan1971@gmail.com*

Abstract

The development of multifunctional polymeric coatings that combine biodegradability, stability, and controlled release capacity is of great importance in modern materials science. In this study, polylactic acid (PLA) was synthesized via an energy-saving microwave-assisted polycondensation route, providing an efficient and sustainable alternative to conventional synthesis methods. The obtained PLA was processed into nanofibrous mats by electrospinning and subsequently deposited onto polyurethane (PU) films to form hybrid multilayer coatings. FTIR spectroscopy indicated the absence of significant chemical interactions between PLA and PU, confirming the preservation of the individual polymer structures. DSC analysis showed the reduction in melting enthalpy which suggests effective integration of the electrospun PLA onto PU substrate and the reduced crystallinity of the hybrid PU/PLA system. SEM micrographs revealed a uniform fibrous morphology of the electrospun PLA layer, providing a coherent and stable coverage of the PU substrate. Mechanical testing of the hybrid coating revealed a tensile strength of 2.9 MPa and an elongation at break of 57%, indicating a balanced combination of strength and flexibility. Beyond pharmaceutical applications, the proposed approach demonstrates potential for environmentally friendly protective and functional coatings in biomedical and packaging technologies. The combination of microwave-assisted synthesis and electrospinning thus represents a sustainable and versatile pathway toward advanced polymer-based multifunctional coatings.

Keywords: *biodegradable polymers; controlled drug release; hybrid PU/PLA coatings; microwave-assisted synthesis*

Introduction

Biodegradable and bio-based polymers are increasingly important for biomedical applications such as wound dressings [1-3], drug delivery [4], and protective coatings. Polylactic acid (PLA) is a biodegradable aliphatic polyester derived from renewable resources, offering high strength and biocompatibility, but its brittleness limits flexibility. Polyurethane (PU), especially when synthesized with bio-based polyols such as polyricinoleate, provides elasticity, toughness, and tenable phase morphology. Hybrid PU/PLA coatings are promising since they integrate the toughness and flexibility of PU with the biodegradability and rigidity of PLA. Moreover, microwave-assisted polymerization represents energy-efficient and sustainable alternative for polymer synthesis, while

electrospinning of PLA nanofibers yields high-surface-area coatings suitable for controlled drug release [5].
Electrospinning has emerged as a versatile technique for fabricating nanofibrous polymer mats with high surface area, porosity, and tunable fiber morphology [6-8]. Such properties are highly beneficial for drug delivery applications, since drugs can be loaded either within the nanofibers or adsorbed on their surface, allowing sustained or stimuli-responsive release. When electrospun fibers are deposited directly onto a flexible polymer substrate, the resulting system can mimic a patch-like configuration, suitable for external applications such as wound dressings or transdermal delivery systems.
In this work, PLA was electrospun directly onto bio-based PU films, yielding PU/PLA hybrid coatings that combine the mechanical flexibility of PU with the biodegradability and nanostructured morphology of PLA. The aim of this study was to develop such a hybrid PU/PLA system using energy-efficient microwave-synthesized PLA and bio-based PU, and to thoroughly characterize its chemical, thermal, morphological, and mechanical properties for advanced coating applications. Moreover, microwave-assisted synthesis routes were employed to ensure sustainability and efficiency in polymer production, aligning with current trends in green materials development.

Experimental

Synthesis of Bio-Based PU

As a soft segment for the preparation of PU, polycatprolactone (Mn=2000 g/mol, from Sigma Aldrich) and polyricinoleate diol synthesized by high-temperature polycondensation of ricinoleic acid with diethylene glycol in the presence of $Ti(iPrO)_4$ catalyst, were used. PU samples were then prepared via a one-pot two-step polymerization using polyricinoleate/PCL (1:1 mol/mol) blends as soft segments and diphenylmethane diisocyanate (MDI) with 1,4-butanediol as chain extender. PU was synthesized with 60% of soft segment content, mixing all components in tetrahydrofuran, as solvent, at 60 °C for 3 hours. The obtained thermoplastic PU was purified and vacuum-dried.

Microwave-assisted synthesis of PLA

Microwave polymerization of L-lactide monomer involves the addition of the dry monomer (5 g) in the evaporating bowls, followed by the addition of tin(II) 2-ethylhexanoate solution (2.81 mg in 1 mL toluene). After the mixture became homogenized toluene was evaporated at 60 °C in vacuum for 6 h. The reaction mixture was then moved to a glass ampoule. Polymerization was performed in a microwave reactor at the frequency of 2.45 GHz. The temperature regulation was carried out by the infrared in-mass measuring system and was maintained at 100 °C. Very short polymerization time was 15 minutes. The obtained PLA was characterized by a yield of 92% and a number-average molecular weight (M_n) of 81,000 g/mol.

Fabrication of Hybrid PU/PLA Coatings

PLA solutions were electrospun into nanofibrous mats and directly deposited onto PU films, yielding PU/PLA multilayer coatings. For electrospinning of pure PLA, 15 wt% solutions of PLA in solvent mixture DCM/DMF (in ratio 4:3 v/v) were prepared. Solutions were homogenized 24 hours on magnetic stirrer at room conditions before electrospinning.
Machine Fluidnatec LE-10 by BioInicia was used for electrospinning. Feed rate 5 ml/h, distance from tip to collector 15 cm and voltage 16 kV were process parameters used for preparation of non-wovens.

Characterization

Fourier transform infrared spectra (FTIR) were recorded by Bomem Hartmann & Braun MB-series, in the wave band range from 400 to 4.000 cm^{-1}. Obtained polymers were milled with KBr before the preparation of tablets under vacuum press.

Differential scanning calorimetry (DSC) measurements were performed using a TA Instruments Q20 DSC (software Universal Analysis from TA Instruments) instrument in the temperature range from 25 to 200°C under nitrogen atmosphere at a heating rate of 10 °C min^{-1}.
PLA nanofiber morphology was analysed on SEM. Scanning electron microscopy (SEM) imaging was done on a SEM Lyra (Tescan) operated at 25 kV.
Mechanical properties of electrospun non-wovens were determined using Tensile Testing Machine Instron 1122, where speed was 1 mm min^{-1} at room conditions. Samples were cut from prepared nonwoven mats in the form of rectangle; with approximate dimensions 10x50 mm.

Results and Discussion

FTIR Analysis

The chemical composition of the polyurethanes, based on polyricinoleate and PCL soft segments, is indicated by a carbonyl band at 1728 cm^{-1}, attributed mainly to free ester C=O of the soft segments but possibly overlapping with free urethane C=O. Ester C–O vibrations appear in the 1100–1200 cm^{-1} region. Characteristic urethane absorptions include an N–H stretching band at 3323–3340 cm^{-1} and an amide II band at 1530 cm^{-1}, Figure 1. The N–H bands were shifted to lower wavenumbers suggesting hydrogen bonding either between the hard segments or between hard segments and soft segments. The peak centered at 1703 cm^{-1} is ascribed to the vibration of hydrogen-bonded carbonyls from both triglyceride ester and urethane groups. FTIR spectrum shows the asymmetrical valence vibrations of the ester C-O-C bond of the aliphatic chain as strong band with a position at 1168 cm^{-1} and symmetrical valence vibrations of C–O–C of the aliphatic chain at 1066 and 1100 cm^{-1}. Other bands that characterize the structure of the used polyester polyols are overlapped by polyurethane bands.

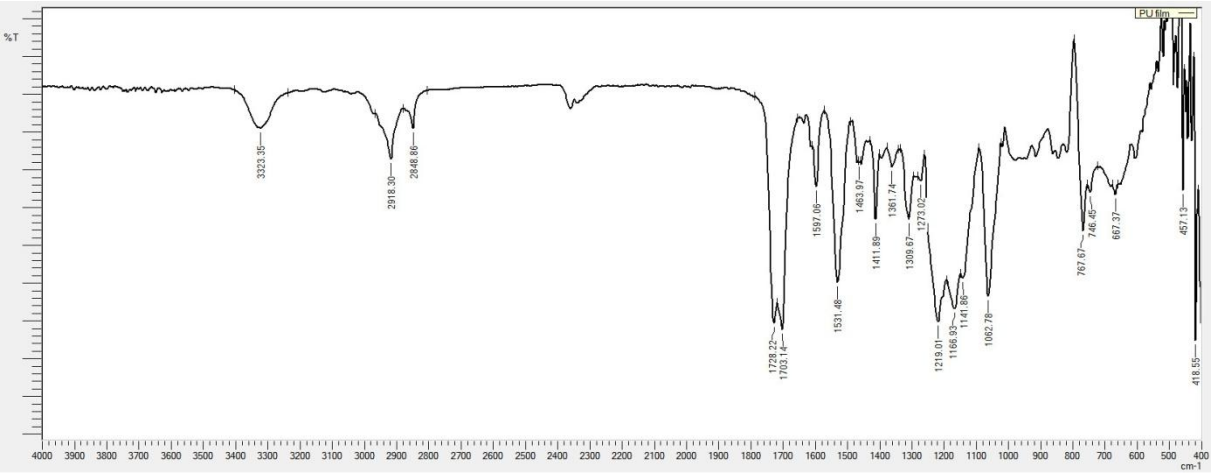

Figure 1. *FTIR spectrum of PU sample.*

The molecular structures of synthesized PLA were estimated by FTIR spectroscopy, Figure 2. Bands at 1751 cm^{-1} (cyclicdilactone C=O valence vibration), 1445 and 1382 cm^{-1} (asymmetric and symmetric bending vibration of C–H from CH_3, respectively) and 930 cm^{-1} (COO ring breathing mode) are characteristic for the FTIR spectra of monomer L-lactide, with band at 1260 cm^{-1} from asymmetric valence vibrations of C–O–C in the lactonic ring and band at 1100 cm^{-1} from symmetric valence vibrations of C–O–C in the lactonic ring. The broad absorption band of the hydroxyl (OH) stretching vibration between 3200 and 3600 cm^{-1} were presented in spectra of synthesized poly(lactide) sample. Bands at 2960 and 2830 cm^{-1} from asymmetric and symmetric valence vibrations of C–H were presented in polymer spectra. The band at 2880 cm^{-1} was attributed to the symmetric valence vibration of C–H from CH_3. As it can be seen from the FTIR spectrum of PLA

the asymmetrical valence vibrations of C–O–C of the aliphatic chain were shifted at 1182 and 1207 cm^{-1}, and symmetrical valence vibrations of C–O–C of the aliphatic chain 1082 and 1100 cm^{-1}, compared with bands at1267 and 1099 cm^{-1}, which appeared in monomer lactide. Band at 1751 cm^{-1} emerges from the valence vibration of C=O of aliphatic ester, whereas the bands at 1454 and 1382 cm^{-1} originated from asymmetric and symmetric bending vibration of C–H from CH_3, respectively. The band at 1260 cm^{-1} from the overlap of C–H bending vibration and C–O–C stretching vibration, was also detected.

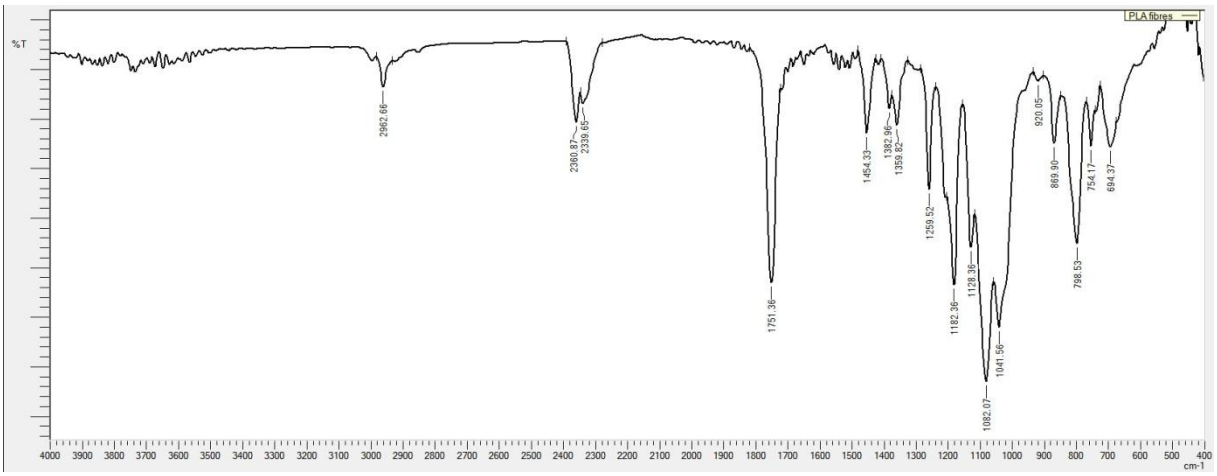

Figure 2. *FTIR spectrum of PLA sample.*

DSC Analysis

The glass transition of the soft segment in PU films was observed at approximately –17 °C, confirming the high chain mobility of the flexible polyester-based domains. However, the glass transitions of the MDI/BDO hard segments were not clearly distinguishable, suggesting that a significant portion of the hard domains remained amorphous. This behavior can be attributed to the use of fatty acid–based polyricinoleate polyols, which introduce dangling chains into the structure. These chains increase the miscibility of hard and soft phases and hinder the formation of well-ordered crystalline hard domains, leading to smaller and more imperfectly packed hard segment regions.

Interestingly, the *Tg* of electrospun PLA fibers (in hibrid PU/PLA materials) was not clearly distinguishable, most likely due to the thin nanofiber morphology and partial amorphous character of the electrospun mats, which suppress the detection of a distinct glass transition. Complex endothermic peak with a maximum at 165 °C was detected, corresponding to the melting of crystalline poly(L-lactide) fibres in hybrid sample, Figure 3. For the PU/PLA hybrid coatings, the overall melting enthalpy was significantly reduced (ΔH_m = 1.42 J/g), indicating that the PLA nanofiber layer contributed only partially to the total crystallinity of the hybrid system. The reduction in melting enthalpy further suggests effective integration of the electrospun PLA within the PU substrate, which limits the extent of crystallization while preserving structural stability.

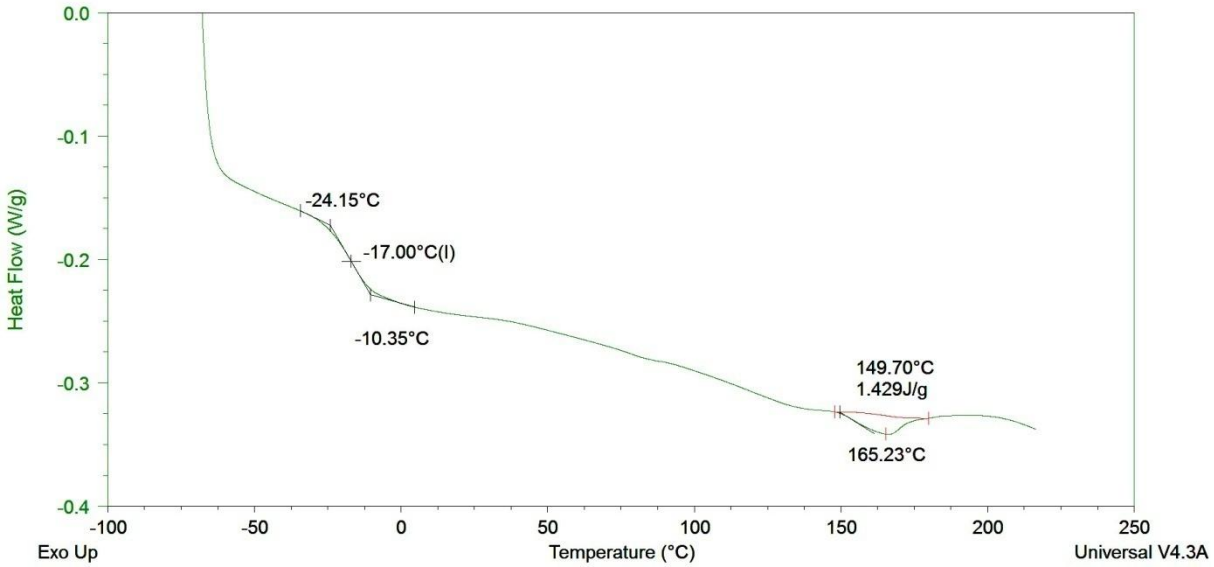

***Figure 3. DSC** thermogram of PU/PLA hybrid sample.*

Morphological analysis

Electrospun PLA nanofibers exhibited uniform fibrous morphology and coherent coverage on PU films, providing a stable substrate with high surface area, favourable for drug release. It can be seen that smooth and uniform fibers without beads and drops were obtained using appropriate process parameters, Figure 4.

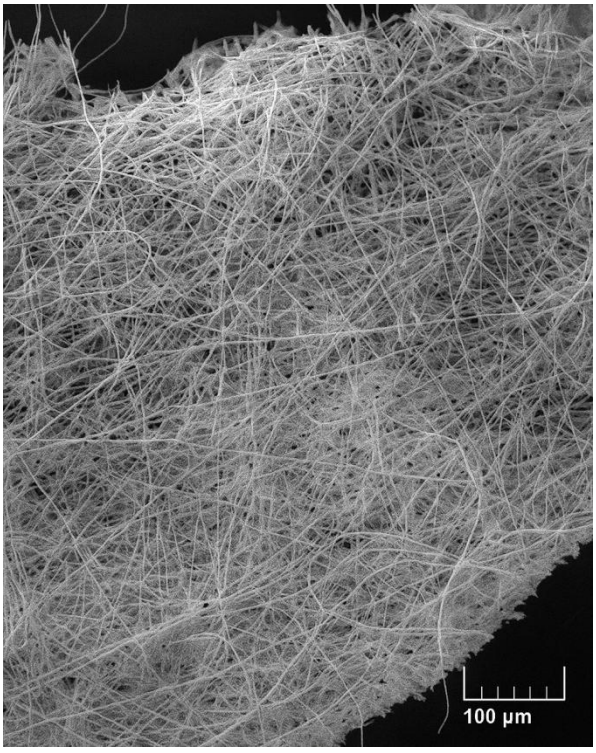

***Figure 4.** SEM micrograph of hybrid PU/PLA sample.*

Analysis of Mechanical Properties

The mechanical performance of the individual polymer components—polyurethane (PU) and polylactic acid (PLA)—was evaluated to understand their contribution to the hybrid PU/PLA system.

Tensile testing revealed the distinct mechanical profiles of the two materials. The PU sample exhibited a tensile strength of approximately 5 MPa and a very high elongation at break of nearly 400%. This behavior is characteristic of a tough and highly elastic material, resulting from the mobility of the long polymer chains in the soft segments.
In contrast, the fibres of pure synthesized PLA demonstrated a tensile strength of 1.6 MPa but a drastically lower elongation at break of less than 10%, confirming its inherently brittle nature. This rigidity is a direct consequence of PLA's semi-crystalline structure and restricted chain mobility, as further confirmed by thermal analysis.
The hybrid PU/PLA material, fabricated by electrospinning PLA nanofibers onto a PU film, exhibited a promising combination of these properties. The mechanical behavior of the hybrid is a synergistic interplay between the two layers. The PU substrate provides the primary flexibility, enabling the entire structure to withstand significant deformation. Upon stretching, the hybrid structure demonstrated a desirable failure mechanism. The initial deformation led to the alignment and unravelling of the PLA nanofibers rather than their immediate fracture. This process allows for efficient stress transfer and energy dissipation. Ultimately, the hybrid material achieved an elongation at break of 57% and a tensile strength of 2.9 MPa. Failure was defined by the fracture of the PLA nanofiber network at this point, which was taken as the ultimate tensile strength of the hybrid construct. It is important to note that the underlying PU film itself, with its much higher inherent elasticity (~400% elongation), had not yet reached its rupture point. This indicates that the electrospun PLA layer provides a reinforcing effect, increasing the strength of the pure PU film, while the PU matrix imparts flexibility to the otherwise brittle PLA fibers, creating a composite material with balanced and satisfactory mechanical properties for advanced coating applications. This indicates that the ductile PU matrix imparts flexibility, while the PLA nanofibers provide strengthening, creating a composite material with balanced and satisfactory mechanical properties for advanced coating applications..
The combination of elastic PU films and rigid electrospun PLA layers resulted in coatings with complementary properties: flexibility, biodegradability, structural stability, and nanostructured morphology suitable for controlled drug release and wound healing.

Conclusion

This study demonstrated that microwave-assisted polymerization provides an energy-efficient route for the synthesis of PLA with controlled crystallinity, while bio-based PU derived from polyricinoleate offers tunable flexibility and toughness. FTIR and DSC analyses confirmed the expected structural features and thermal transitions, including the suppressed glass transition of PLA nanofibers and the reduced crystallinity of the hybrid PU/PLA system. SEM imaging revealed uniform nanofiber morphology with coherent coverage of PU substrates, while mechanical testing highlighted the synergistic performance of the hybrid, combining the ductility of PU with the reinforcing effect of PLA fibers. The hybrid coating exhibited a tensile strength of 2.9 MPa and an elongation at break of 57%, demonstrating a successful compromise between the mechanical properties of its individual components. The developed PU/PLA hybrid coatings can be regarded as patch-like systems, offering both flexibility and controlled drug release capacity. Such materials hold strong potential for biomedical applications, particularly in wound dressings and transdermal delivery platforms, while also supporting sustainability goals through the use of energy-saving synthesis methods and renewable resources.

Acknowledgements

This work was supported by the Ministry of Scientific and Technological Development and Higher Education of theRepublic of Srpska, through the project ''Development of New Systems for Controlled Drug Delivery based on Biodegradable Polymers'', contact number 19.032/961-91/24,

and the NATO SPS program, project G6031-"Wearable Smart Patches for Multimodal Wound Healing - DRESWOUTRE" for financial support.

References

1. Gültekin, G., Atalay-Oral, Ç., Erkal, S., Şahin, F., Tantekin-Ersolmaz, S. B., & Güner, F. S. (2019). Fatty acid-based polyurethane films for wound dressing applications. *Journal of Materials Science: Materials in Medicine 20*, 421–43 https://doi.org/10.1007/s10856-019-6244-8
2. Filatova, K., Domincova Bergerova, E., Kazantseva, N., Masar, M., Suly, P., Sopik, T., Cisar, J., Durpekova, S., & Sedlarik, V. (2023). Design and fabrication of electrospun PLA-based silica-modified composite nanofibers with antibacterial properties for perspective wound treatment. *Polymers, 15*(17), 3500. https://doi.org/10.3390/polym15173500
3. Abolhassani, S., Alipour, H., Alizadeh, A., Nemati, M. M., Najafi, H., & Alavi, O. (2022). Antibacterial effect of electrospun polyurethane-gelatin loaded with honey and ZnO nanoparticles as potential wound dressing. *Journal of Biomaterials Applications*. Advance online publication. https://doi.org/10.1177/15280837211069871
4. Gajić, I., Stojanović, S., Ristić, I., Ilić-Stojanović, S., Pilić, B., Nešić, A., Najman, S., Dinić, A., Stanojević, L., & Urošević, M. (2022). *Electrospun Poly(lactide) fibers as carriers for controlled release of Biochanin A*. *Pharmaceutics, 14*(3), 528. https://doi.org/10.3390/pharmaceutics14030528
5. Nikolic, L., Ristic, I., Adnadjevic, B., Nikolic, V., Jovanovic, J., Stankovic, M. (2010). Novel Microwave-Assisted Synthesis of Poly(D,L-lactide): The Influence of Monomer/Initiator Molar Ratio on the Product Properties. *Sensors*, *10*(5), 5063-5073. https://doi.org/10.3390/s100505063
6. Magiera, A., Markowski, J., Menaszek, E., & others. (2017). PLA-based hybrid and composite electrospun fibrous scaffolds as potential materials for tissue engineering. *Journal of Nanomaterials*, 2017, Article 9246802. https://doi.org/10.1155/2017/9246802
7. Yan, L., Si, S., Chen, Y., Yuan, T., Fan, H., Yao, Y., Zhang, Q. (2011). Electrospun in-situ hybrid polyurethane/nano-TiO_2 as wound dressings. *Fibers and Polymers, 12*(2), 207-213. https://doi.org/10.1007/s12221-011-0207-0
8. Pahlevanneshan, Z., Deypour, M., Kefayat, A., Rafienia, M., Sajkiewicz, P., Esmaeely Neisiany, R., & Enayati, M. S. (2021). Polyurethane-nanolignin composite foam coated with propolis as a platform for wound dressing: synthesis and characterization. *Polymers, 13*(18), 3191. https://doi.org/10.3390/polym13183191