U.P.B. Sci. Bull., Series B, Vol. 87, Iss. 1, 2025 ISSN 1454-2331

ENHANCING MECHANICAL PROPERTIES OF POLYUREA THROUGH CELLULOSE NANO CRYSTALS (CNF) REINFORCEMENT

Kadir DUMAN[1], Madalina Ioana NECOLAU[2], Anamaria ZAHARIA[3], Horia IOVU[4]

This research introduces a new method designed to enhance the mechanical performance of polyurea by integrating cellulose nanofibers (CNF). The process begins with the ultrasonic dispersion of dried CNF in an isocyanate solution, followed by mixing it with polyol and subjecting the mixture to a heating process, ensuring the proper incorporation of CNF into the polyurea matrix. The mechanical and thermal properties of the resulting materials were evaluated using dynamic mechanical analysis (DMA), differential scanning calorimetry (DSC), and thermogravimetric analysis (TGA), which provided valuable insights into their thermal stability and behavior. Additional morphological characteristics were examined using scanning electron microscopy (SEM). Comparative studies of the films made from both modified and unmodified polyurea demonstrated significant improvements in mechanical properties. Specifically, the inclusion of CNF led to a 24.4% enhancement in tensile strength and an increase in modulus, especially at the optimal CNF concentrations. However, a further increase in CNF content resulted in reduced elongation at break, indicating a loss of ductility.

Keywords: Cellulose nano fibers, reinforced polyurea, nanocomposite materials, sustainable nanocomposites

1. Introduction

Cellulose, a widely abundant organic polymer, accounts for nearly 40% of the total plant biomass on Earth, with global production estimates varying between 10 and 100 billion tons annually. Its molecular structure, characterized by

---

[1] PhD student, Advanced Polymer Materials Group, National University of Science and Technology POLITEHNICA Bucharest, Romania; e-mail: kadir.duman@stud.chimie.upb.ro

[2] PhD student, Advanced Polymer Materials Group, National University of Science and Technology POLITEHNICA Bucharest, Romania, e-mail: madalina.necolau@upb.ro; Academy of Romanian Scientists, Ilfov 3, 050044 Bucharest, Romania

[3] Advanced Polymer Materials and Polymer Recycling Group, National Institute for Research and Development in Chemistry and Petrochemistry-ICECHIM, Bucharest, Romania, e-mail: anamaria.lungu1984@gmail.com

[4] Prof., Advanced Polymer Materials Group, National University of Science and Technology POLITEHNICA Bucharest, and Academy of Romanian Scientists, Bucharest, Romania, e-mail: horia.iovu@upb.ro

alternating regions of crystalline and amorphous formations, plays a critical role in determining its mechanical properties. The polymer is composed of repeating units of d-glucopyranose, connected by β-1,4-glycosidic linkages. The level of polymerization varies depending on the source and processing techniques, giving cellulose its remarkable structural versatility and adaptability, making it suitable for a wide array of functional applications [1-5]. Among cellulose derivatives, cellulose nanofibrils (CNFs) are notable for their semi-crystalline nature and fibrillar network, which impart good flexibility and strength. These properties position CNFs as advantageous reinforcing agents within polymer composites, relevant for a spectrum of applications from packaging with antibacterial properties to drug delivery systems, owing to their transparency, strength, and biocompatibility [6,7].

The incorporation of cellulose nanofibers (CNFs) into composite materials has garnered significant interest due to their potential for enhancing mechanical properties. When integrated into polymer matrices, they contribute to improved material uniformity, reduced defect rates, and superior mechanical performance. The versatile applications of CNFs span across various industries, from traditional material engineering to sectors such as energy, environmental sciences, and biomedicine, where their unique properties are harnessed to create advanced technologies. Nevertheless, integrating CNFs into polymers presents challenges. Their hydrophilic nature leads to difficulties in suspension in aqueous environments and impedes dispersion in hydrophobic polymer systems. These limitations can obstruct the full potential of CNFs as reinforcing agents. To overcome these challenges, researchers have focused on breaking down cellulose fibers into nanocellulose and utilizing surface modification techniques. By altering the surface properties of CNFs, their hydrophobicity and compatibility with different polymer matrices have been enhanced. This engineering results in better dispersion, reducing aggregation and ensuring more uniform distribution throughout the composite materials [1,2].

In polymer nanocomposites, cellulose nanofibers (CNFs) significantly improve both tensile strength and modulus, largely due to their high aspect ratio and their capacity to efficiently distribute applied stress. For example, adding 5% by weight of CNFs into polylactic acid (PLA) substantially enhances its rigidity and tensile properties. Similarly, incorporating CNFs into epoxy composites enhances thermal stability and mechanical performance, further demonstrating their effectiveness in reinforcing polymer matrices when paired with targeted surface treatments and advanced dispersion techniques [3-6]. While extensive research has focused on utilizing CNFs across various polymer matrices, their specific application within polyurea systems remains underexplored. Polyurea, known for its exceptional mechanical properties, provides a promising platform for integrating CNFs. This study seeks to bridge this gap by exploring how CNF inclusion in polyurea matrices can be leveraged to improve mechanical performance for broader applications.

Conventional approaches for incorporating CNFs into polymer matrices often utilize solvent or aqueous methods, which are not suitable for polyurea because of the high reactivity of isocyanate groups with water. In this study, we addressed these challenges by adopting a method where CNFs are dispersed directly into low-viscosity monomeric 4,4'-methylene diphenyl diisocyanate (MDI). By employing a carbodiimide-modified version of 4,4'-methylene diphenyl diisocyanate, we were able to achieve both mechanical blending and chemical bonding of CNFs within the polyurea matrix, thereby enhancing the overall properties of the composite [1].

2. Materials and methods

2.1 Materials

Cellulose Nanofibers (CNF), obtained in the form of a dry powder with a moisture content of less than 4.0%, were sourced from Nanografi. Prior to their use, CNFs were further dried at 120°C for four hours to ensure a residual moisture content of less than 2%. This dehydration step is critical for preventing any adverse reactions with isocyanate groups in the polyurethane matrix.

The polyurethane matrix was formulated using high-quality raw materials. Polyol (Desmophen 2061 BD, OH value = 56 KOH/g) was obtained from Bayer, while Isocyanates (LUPRANAT MI, 250 g/mol; isocyanate groups content (NCO) = 33.5 g/100 g; purity 99.5%), and Lupranat MM 103 (NCO content = 29.5 g/100 g) were sourced from BASF, Germany.To facilitate the processing and application of CNFs in the polymer matrix, additional materials were used. Propylene Propylene carbonate, used as a solvent (99.7% purity), and polyetheramine (total amine =1.05 meq/g) - a difunctional primary amine, were acquired from Huntsman. Curing agents, which are pivotal for achieving the required cross-linking density and imparting desirable mechanical properties to the composite, were chosen as follows: ETHACURE 100 (178 g/mol, equivalent weight with isocyanates = 89.1) and ETHACURE 300 (214 g/mol, equivalent weight with isocyanates = 107) from Albemarle. For the efficient processing and stability of the composite, BYK A 530 was utilized as a defoamer, and Disperbyk 2152 served as a dispersing agent, both sourced from BYK, Germany. Additionally, SILIPORITE NK10AP from Arkema was used as a molecular sieve and moisture absorber for the amine component.

2.1.2 Modified polyurea preparation and film casting

To prepare the prepolymer, 0.015 parts of pre-dried CNF were placed into a reaction flask fitted with a mechanical stirrer. Subsequently, 0.1 parts of

Lupranat MM 103 were added. Initially, the mixture was left undisturbed to allow for reaction sampling. Stirring and heating to 80°C began following the initial mixture. The temperature and stirring speed were kept consistent, with samples taken every 30 minutes. FT-IR spectroscopy was utilized to track the progress of the reaction by observing the reduction in the intensity of the characteristic peaks for the isocyanate groups (NCO). This process continued for around four hours, after which no further decrease in the NCO peaks was detected.

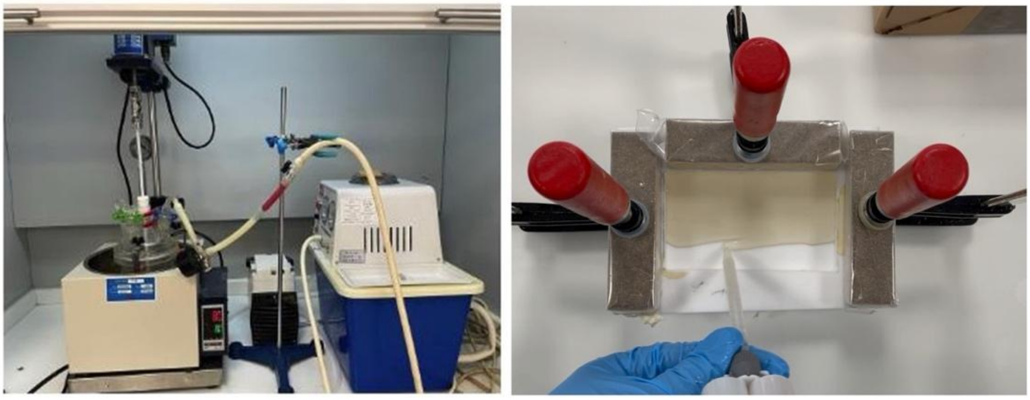

Fig. 1. The reactor used for prepolymer synthesis and the film casting process

Once the NCO peaks stabilized, indicating the end of the first reaction phase, 0.3 part of LUPRANAT MI and 0.51 part of Desmophen 2061 BD were added to the flask. Heating and stirring were continued under the same conditions as earlier, and the reaction was monitored in a similar manner to ensure complete integration and reaction of the components.

After the reaction was completed, as confirmed by stable spectroscopy readings, the temperature of the mixture was lowered to 40°C. At this point, 0.045 parts of propylene carbonate were added and thoroughly stirred into the mixture to ensure uniform distribution and finalize the chemical properties. The final step involved cooling the mixture to room temperature under a nitrogen atmosphere. Throughout the entire preparation, all additions and samplings were performed under a nitrogen blanket to maintain an inert environment, preventing any premature reactions or degradation of the reactants and product.

Preparation of Amine Component: To prepare the amine component, a precise formulation of additives and curing agents was mixed under controlled conditions. The components included 1 part of SILIPORITE NK10AP, 0.5 part of BYK A 530 (a defoamer), 0.1 part of Disperbyk 2152, 28.4 parts of ETHACURE 100, and 30 parts of ETHACURE 300—both serving as curing agents—along with 40 parts of Desmophen 2061 BD, which acted as the base polyol. The mixture was combined at room temperature using a mechanical stirrer. To further reduce the occurrence of bubbles, which are typical in such mixtures, a vacuum was applied during the mixing process.

The prepolymer and amine components were blended using a double cartridge system equipped with a static mixer. Both components, A and B, were dispensed at equal temperatures into a 4 mm thick Teflon mold using a cartridge gun. The film was cured at 23°C and 50% humidity for a duration of 4 hours, followed by a conditioning process in a 50°C oven for 7 days. Four different samples were prepared under these conditions and the following samples were obtained:

Table 1.

Composition and description of polyurea based composites

Sample name	**Detail**	**CNF amount, %**
PU	Blank prepolymer	0
PU-CNF-0.5%	0.5% CNF grafted hybrid polyurea	0.5
PU-CNF-1%	1% CNF grafted hybrid polyurea	1
PU-CNF-1.5%	1.5% CNF grafted hybrid polyurea	1.5

2.2 Methods

The attachment of cellulose nanofibrils (CNF) to monomeric MDI and the formation of urethane bonds were validated using Fourier Transform Infrared Spectroscopy (FT-IR). For this analysis, the spectral data was obtained using a Bruker Alpha II spectrometer, which operated in attenuated total reflection (ATR) mode. This technique is particularly advantageous for studying surface chemistry and chemical bond formation. A Germanium (Ge) crystal, known for its wide spectral range and high refractive index, was used in the ATR setup, making it particularly suitable for examining a variety of materials, including organic polymers and nanocomposites.

Each spectrum consisted of 32 scans, providing sufficient data for comprehensive analysis. The spectra were recorded at a resolution of 4 cm^{-1} and covered a range from 400 to 4000 cm^{-1}, allowing for a detailed examination of functional groups, specifically focusing on -N=C=O groups from isocyanates and the urethane groups that formed as a result of the reaction. The observed reduction in -N=C=O peaks confirmed the successful formation of urethane bonds, thereby demonstrating the efficient integration of CNFs into the polyurea matrix.

Additionally, the identification of other functional groups was confirmed using Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA). DSC measurements were performed with a Netzsch 204 F1 Phoenix instrument, where samples were heated from room temperature to 300°C at a controlled rate of 10°C per minute under a nitrogen flow of 20 mL/min in aluminum crucibles. TGA analyses were carried out using a TG 209 F1 Libra instrument, with samples heated from 20°C to 700°C at a rate of 10°C per minute under a nitrogen atmosphere (20 mL/min). These techniques provided comprehensive data on the composition and thermal properties of the synthesized monomers.

Dynamic Mechanical Analysis (DMA) was conducted using a TRITEC 2000 Bdevice from Triton Technology, Ltd., now Mettler Toledo. The tests were performed in a single cantilever bending mode at a frequency of 1 Hz, with samples being heated across a temperature range from -80°C to 0°C at a rate of 5°C per minute. Mechanical testing was performed using a universal mechanical tester (Instron, Model 3382, Norwood, MA, USA) under controlled humidity conditions (45–50%) at a test speed of 1 mm/min. The sample dimensions were approximately 10 × 1 cm, and a minimum of three specimens were evaluated for each polyurea sample, with the average results reported.

Further analysis of the morphology of the functionalized nanocellulose-based nanocomposites was carried out using scanning electron microscopy (SEM). The samples were coated with a thin layer of gold and examined using a Quanta 200 Environmental Scanning Electron Microscope (FEI-Philips), equipped with a tungsten electron source operating in low vacuum mode at an accelerating voltage of 30 kV.

3. Results and discussions

3.1. FT-IR analysis

In the process of optimizing the polyurea formulation, FT-IR spectroscopy was utilized to track the formation of urethane bonds, confirming the interaction between the hydroxyl groups in the CNFs and the isocyanate groups in MDI. The appearance of characteristic urethane peaks further validated these interactions. This result aligns with previous findings by Leng et al. and Gunashekar et al., who reported similar absorption bands near 3300 cm^{-1} for hydroxyl groups, as well as peaks around 3200 cm^{-1} and 1720 cm^{-1}, which correspond to urethane NH stretching and carbonyl groups, respectively. This confirmed the successful formation of the desired chemical structure [2-4]

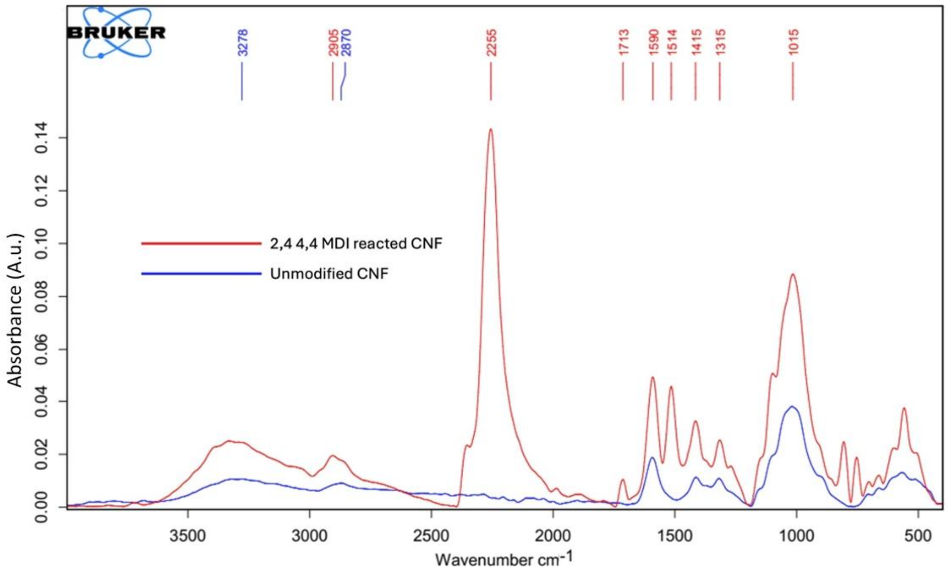

Fig. 2. FT-IR spectra of unmodified and MDI reacted CNF

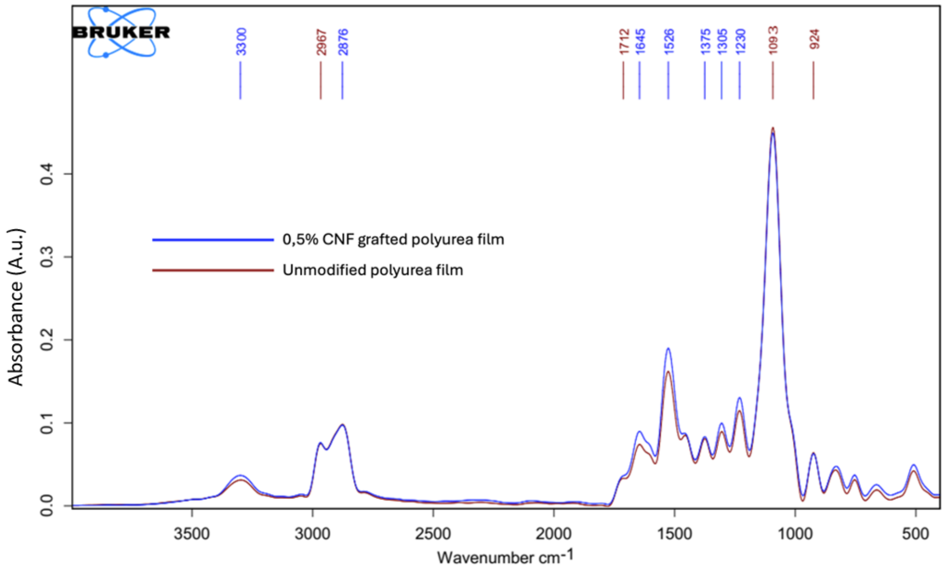

Fig. 3. FT-IR spectra of unmodified and CNF grafted polyurea films

The peak at 1645 cm^{-1} is typically associated with the C=O stretching vibrations found in the amide groups of urea. The increased intensity of this peak in our spectra indicates enhanced hydrogen bonding within the matrix, likely facilitated by the hydroxyl groups present on the CNFs. These hydroxyl groups interact with the isocyanate (NCO) groups from MDI, forming urethane linkages. However, it is important to note that free urethane bonds are usually detected at a different wavelength. According to the findings of Guo and colab. the carbonyl stretch (C=O) for free urethane typically appears near 1730 cm^{-1} in polyurethane matrices. Thus, the peak at 1645 cm^{-1} observed in this study suggests interactions related to the urea structure within the matrix, rather than direct evidence of free urethane bond formation [3].

This observation aligns with the expected behavior when CNFs are introduced into polyurea systems, suggesting that the hydroxyl groups of CNF are likely reacting with the MDI's isocyanate groups to contribute to the matrix's structural integrity, rather than forming new free urethane structures.

The spectral shoulder observed at 1712 cm^{-1} falls within the expected range for hydrogen-bonded urethane groups. As Barlow et al. noted, hydrogen-bonded urethane carbonyl groups frequently appear as a shoulder near 1710 cm^{-1}. The slight rise at 1712 cm^{-1} in our spectra likely signifies the presence of these hydrogen-bonded urethane structures, confirming the interaction between the hydroxyl groups of CNFs and the isocyanate-derived urethane linkages within the polyurea matrix [4].

The peak observed near 3300 cm^{-1}, corresponding to N-H stretching vibrations in amides, indicates a more robust hydrogen bonding network within the polyurea matrix. The increase in intensity of this peak following the addition of CNFs suggests stronger interactions within the hybrid matrix, which likely contributes to enhanced mechanical properties and stability. These findings align with other studies on vibrational wavenumbers, highlighting the importance of such spectral features in identifying molecular interactions, particularly in hydrogen-bonded systems [5,6].

These spectral features collectively validate the hypothesis that CNF enhances the structural integrity and mechanical properties of the polyurea system through improved interfacial bonding and load transfer capabilities.

3.2. Mechanical Properties

The mechanical properties of polyurea with varying concentrations of CNF were investigated to assess the impact of CNF on the matrix's mechanical behavior. Table 2 presents the Young's modulus and tensile strain obtained from universal mechanical testing for the neat polyurea (PU) and its composites with 0.5%, 1%, and 1.5% CNF content.

Table 2

Mechanical test results obtained from the universal mechanical tester

Sample	**Young modulus (MPa)**	**Tensile strain (%)**
PU	59.6	14
PU-CNF-0.5%	78.7	17
PU-CNF-1%	58.4	22
PU-CNF-1.5%	43.5	33

Incorporating 0.5% CNF into the polyurea resulted in a significant increase in Young's modulus, rising from 59.6 MPa in pure polyurea to 78.7 MPa in the composite. This enhancement in stiffness is likely attributed to improved load transfer and stress distribution facilitated by the CNF, which provides additional nucleation sites for the urethane and urea hard segments, leading to a more rigid structure. Additionally, the tensile strain increased from 14% to 17%, reflecting an improvement in the material's ductility, with CNF likely acting as a reinforcing phase within the polyurea matrix [13]. At a CNF concentration of 1%, the Young's modulus slightly decreased to 58.4 MPa compared to neat PU. This decrease could be related to agglomeration effects at higher CNF loadings, where CNF aggregates create stress concentration sites and diminish the composite's stiffness.

However, the tensile strain increased to 22%, reflecting better energy dissipation and plastic deformation capabilities, possibly due to a more complex interfacial bonding between CNF and the polyurea matrix.

The composite containing 1.5% CNF exhibited a further reduction in Young's modulus to 43.5 MPa, likely due to the excessive CNF content, which may lead to more prominent defect sites and reduced efficiency in stress transfer. Despite this, the tensile strain saw a significant rise to 33%, suggesting that at higher CNF concentrations, the composite can undergo more extensive plastic deformation before failure. This behavior aligns with the formation of a percolating network of CNF, which can shift and realign under stress, promoting increased material stretch.

The observed trend of increasing tensile strain with higher CNF content across all samples is likely due to the ductilizing effect of CNF, along with potential changes in the polyurea's microstructure. The initial increase in Young's modulus followed by a decrease as CNF content rises demonstrates the complex interplay between reinforcement and the aggregation effects of CNF within the polyurea matrix.

3.3. Thermal Properties

Thermogravimetric analysis (TGA) was utilized to evaluate the thermal degradation characteristics of both pure polyurea and its composites containing cellulose nanofibers (CNF). The temperatures corresponding to 3%, 5%, and 10% weight loss ($T_{d3\%}$, $T_{d5\%}$, $T_{d10\%}$), residual mass percentage, and peak decomposition temperatures (T_{max} from DTG) are detailed in Table 3.

Table 3

TGA results for polyurea matrix and CNF-based composites

Sample	**$T_{d3\%}$ (°C)**	**$T_{d5\%}$ (°C)**	**$T_{d10\%}$ (°C)**	**Residual mass (%)**	**T_{max} (°C) from DTG**	
PU	248.7	265.3	287.7	4.06	289.9	380.8
PU-CNF-0.5%	252.5	267.9	288.1	5.14	306.3	384.8
PU-CNF-1%	249.1	264.3	285.7	4.70	303.1	385.2
PU-CNF-1.5%	254.2	268.7	286.8	5.42	290.8	386.3

The observed incremental increases in $T_{d3\%}$, $T_{d5\%}$, $T_{d10\%}$ for CNF-enhanced composites imply improved thermal stability compared to neat PU. Such an increase, particularly noted in the PU-CNF-0.5% composite, could be indicative of the reinforcing effect of CNFs at lower concentrations. This is supported by research indicating that nanofillers can enhance thermal stability by facilitating char formation that acts as a barrier during thermal decomposition [7].

The augmentation of residual mass in composites with CNFs suggests that CNFs contribute to char residue, thereby providing structural integrity at elevated temperatures. This aligns with literature findings that have shown an increase in char yield to correlate with enhanced thermal stability in polymer composites. Such enhancements are particularly evident in systems where nanofillers facilitate char formation acting as a thermal barrier during decomposition [8].

A higher T_{max} indicates the temperature at which the composite can resist thermal degradation, with the PU-CNF-1.5% composite showing the highest T_{max}. This increase suggests that the presence of CNF could effectively slow down thermal decomposition, likely by creating a barrier to volatile degradation products. In conclusion, incorporating CNFs into polyurea matrices appears to have a stabilizing influence on the composite's thermal properties.

These findings propose that CNFs can enhance the thermal endurance of polyurea, potentially making them suitable for high-temperature applications. Future work should aim to elucidate the underlying mechanisms of thermal stabilization provided by CNFs and explore the potential of such composites in thermally demanding environments.

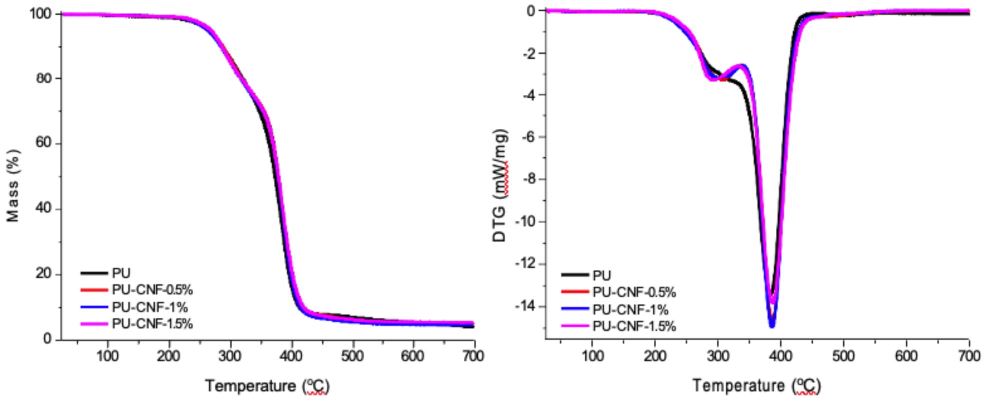

Fig. 4. TGA and DTG curves for blank polyurea materials and CNF reinforced composites

Therefore, the findings indicate that incorporating CNFs into a polyurea matrix can significantly improve the material's mechanical and thermal properties. However, enhancements in attributes such as modulus, tensile strength, and thermal stability are strongly influenced by the CNF content and its dispersion within the matrix. This study highlights the importance of carefully balancing the concentration of nanofillers and their distribution to optimize composite materials. These results offer deeper insights into the material science of CNF-reinforced polyurea, which is essential for the development of advanced materials with custom-tailored properties for specific applications.

3.4. Dynamic Mechanical Analysis (DMA)

The DMA curves illustrate the relationship between the storage modulus and tan delta across varying temperatures for both pure polyurea and its CNF composites. The storage modulus indicates the stiffness of the materials, while the tan delta peak corresponds to the glass transition temperature (Tg), where the material transitions from a rigid, glassy state to a more flexible, rubbery state.

Initially, the storage modulus of all samples is elevated, reflecting a glassy and rigid state at lower temperatures. As the temperature increases, a reduction in the storage modulus is observed, marking the beginning of the glass transition region, where the polymer starts to soften. The presence of CNF helps to maintain higher modulus values compared to pure polyurea, particularly in the PU-CNF-0.5% composite, indicating that CNF incorporation contributes to a stiffer composite in the glassy region.

The addition of CNF causes the tan delta peak to shift to lower temperatures. This shift suggests that CNF composites transition to a rubbery state at a lower temperature compared to pure polyurea. This effect is likely due to CNFs influencing the mobility of the PU matrix chains, allowing for an earlier transition.

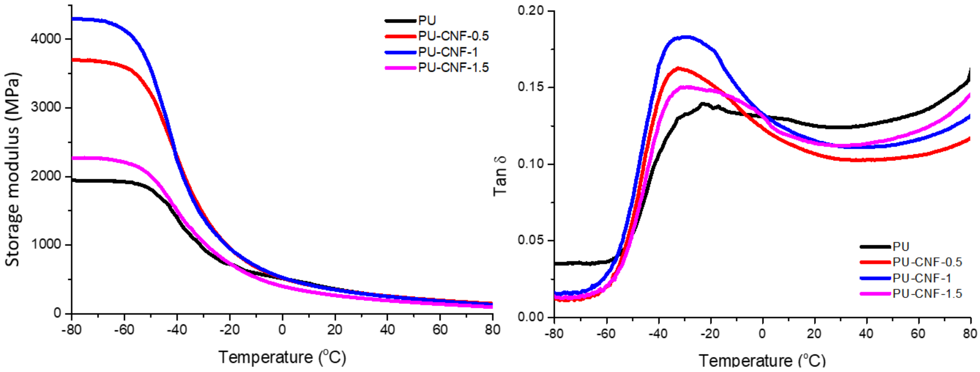

Fig. 5. DMA analysis of blank polyurea sample and CNF reinforced polyurea composites

The Tg values derived from DMA align with the onset of the tan delta peak and exhibit a decrease with the addition of CNF. This decrease corresponds to the earlier onset of chain mobility in the composite materials when compared to pure polyurea.

3.5. Differential scanning calorimetry analysis (DSC)

The DSC analysis provides two thermal transitions, namely, T_g soft and T_g hard. The T_g soft likely corresponds to the initial relaxation of the softer segments of the polyurea matrix, while the T_g hard may be associated with the relaxation of the more constrained, harder segments. It was noted that the T_g values (both soft and hard) from DSC are higher than those obtained from DMA, which is common due to the different testing methods and parameters. The DMA results correlate with the DSC analyses and demonstrate that CNF reinforcement impacts both the thermal and mechanical properties of polyurea. The inclusion of CNF lowers the glass transition temperature, as indicated by the shift in tan delta peaks in the DMA results and the reduced Tg values observed in the DSC analysis. Additionally, the incorporation of CNF enhances the stiffness of the composites in their glassy state, as evidenced by the increased storage modulus shown in the DMA results.

Table 4

Glass transition temperatures (Tg) data obtained from DMA and DSC curves

Sample	**T_g (°C) from DMA**	**T_g soft (°C) from DSC**	**T_g hard (°C) from DSC**
PU	-24.02	-23.6	13.6
PU-CNF-0.5%	-31.31	-26.3	22.0
PU-CNF-1%	-31.97	-24.7	22.1
PU-CNF-1.5%	-32.70	-27.5	22.1

These results suggest that CNF not only influences the thermal behavior of PU composites but also enhances their mechanical performance, especially in the glassy state. The careful optimization of CNF content can potentially tailor the material properties for specific application requirements where improved mechanical performance at lower temperatures is desirable.

3.6. SEM Analysis and Mechanical Properties Correlation

SEM analysis of polyurea and CNF reinforced composites highlights the nanoscale structural changes and their impact on mechanical performance. The SEM images show that as CNF content increases, there is a noticeable change in the surface morphology of the samples, corresponding directly with enhancements in mechanical properties.

For pure polyurea, SEM analysis reveals a relatively smooth surface with minor imperfections. The addition of 0.5% CNF increases surface roughness, indicating improved distribution within the matrix and more efficient load transfer at the polymer-filler interface, thereby enhancing the composite's modulus. At 1% CNF, further increases in surface roughness correspond with optimal filler-matrix interaction, resulting in significant tensile strength improvements. However, at 1.5% CNF, the analysis shows evidence of CNF agglomeration, leading to uneven stress distribution and a decline in mechanical properties, including reduced modulus and lower elongation at break.

These SEM findings, together with mechanical test results, demonstrate that while CNFs can significantly enhance mechanical performance through improved load transfer and interfacial bonding, excessive CNF content may result in filler agglomeration, negatively impacting the composite’s properties. This indicates that a careful balance of CNF content is crucial to maximize the reinforcing effects without compromising the integrity of the material.

Achieving this balance is essential for developing advanced composites with superior mechanical properties. The SEM image of the pure polyurea, the surface appears relatively smooth with occasional imperfections. Upon the addition of 0.5% CNF, the composite surface exhibits a marked increase in rugosity, indicating that CNFs are well-dispersed within the matrix and create a more textured surface.

This topographical change is associated with the mechanical interlocking that occurs at the polymer-filler interface, enhancing load transfer capabilities and improving the modulus.

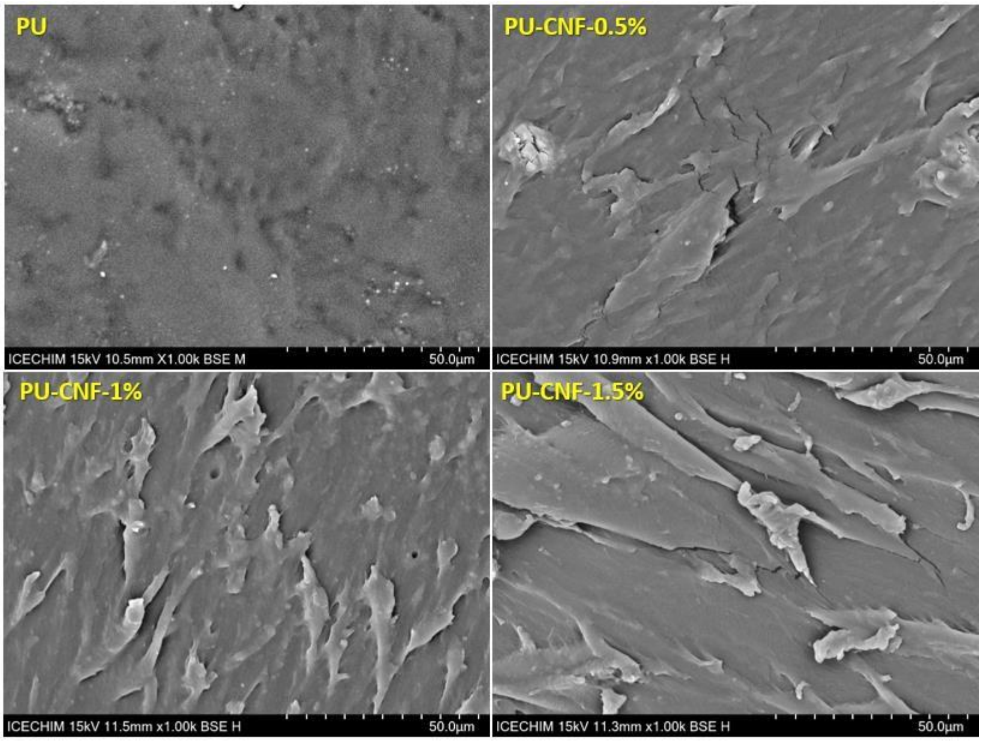

Fig. 6. SEM images of blank polyurea sample and CNF reinforced polyurea composite

4. Conclusions

The comprehensive analysis of CNF-reinforced polyurea composites in this study highlights the essential role of CNFs in enhancing both the mechanical and thermal properties of polyurea. FT-IR spectroscopy confirmed the chemical integration of CNFs into the polyurea matrix, primarily through urethane bond formation. This chemical bonding is crucial for improving the structural integrity and load-bearing capacity of the matrix.

Our experimental data demonstrate that the optimal CNF loading, which maximizes mechanical benefits without compromising processability and thermal properties, is approximately 1% by weight. At this concentration, CNFs are well-dispersed within the matrix, as verified by SEM analysis, which correlates with marked improvements in tensile strength and modulus. Conversely, higher CNF concentrations lead to agglomeration, which adversely affects mechanical performance by creating stress concentration sites.

Thermal analysis, including TGA and DTG techniques, complemented by DSC and DMA studies, outlines a comprehensive profile of the thermal behavior of the composites. The results indicate that while CNFs enhance the thermal stability of polyurea, excessive CNF content can diminish the glass transition temperature, highlighting the need for precise control over CNF dispersion.

The synergistic enhancement of mechanical strength and thermal stability underscores the potential of CNF-reinforced polyurea composites for high-performance applications. This research paves the way for future investigations aimed at optimizing CNF dispersion to prevent agglomeration at higher loadings and exploring the combined effects of CNFs with other reinforcing agents. Such efforts could further improve the properties of materials used in critical applications, such as personal protective equipment.

Acknowledgement

This research study was supported by a grant of Academy of Romanian Scientists, Sustainable materials based on polybenzoxazines with self-healing properties for electronic applications (Eco-HEAL), AOSR -TEAMS – III, 2024-2025. The research group from ICECHIM gratefully acknowledges the opportunity provided by the Ministry of Research, Innovation and Digitalization, (Romanian Funding Agency UEFISCDI), through supporting institutional project no. 2N/03.01.2023 (PN 23.06.01.01. AQUAMAT)

REFERENCES

1. Nozaki, A. P. M., Lona, L. Comparison between cellulose nanocrystal and microfibrillated cellulose as reinforcement of poly (vinyl acetate) composites obtained by either in situ emulsion polymerization or a simple mixing technique. Cellulose, 28, 2273-2286 (2021).
2. Le Gars, M., Bras, J., Salmi-Mani, H., Ji, M., Dragoe, D., Faraj, H., Domenek, S., Belgacem, N., & Roger, P. Polymerization of glycidyl methacrylate from the surface of cellulose nanocrystals for the elaboration of PLA-based nanocomposites. Carbohydrate polymers, 234, 115899 (2020).
3. Sakakibara, K., Morikiti, Y., Yano, H., & Tsujii, Y. Strategy for the Improvement of the Mechanical Properties of Cellulose Nanofiber-Reinforced High-Density Polyethylene Nanocomposites Using Diblock Copolymer Dispersants. ACS Applied Materials & Interfaces, 9(50), 44079–44087 (2017).
4. Barhoum, A., Li, H., Chen, M., Cheng, L., Yang, W., & Dufresne, A. Emerging Applications of Cellulose Nanofibers. In Barhoum, A., Bechelany, M., & Makhlouf, A. (Eds.), Handbook of Nanofibers. Springer, Cham, 1131–1156 (2019).
5. Nakagaito, A. N., Fujimura, A., Sakai, T., Hama, Y., & Yano, H. Production of microfibrillated cellulose (MFC)-reinforced polylactic acid (PLA) nanocomposites from

sheets obtained by a papermaking-like process. Composites Science and Technology, 69, 1293-1297 (2009).

6. Jonoobi, M., Harun, J., Mathew, A. P., & Oksman, K. Mechanical properties of cellulose nanofiber (CNF) reinforced polylactic acid (PLA) prepared by twin screw extrusion. Composites Science and Technology, 70, 1742-1747 (2010).
7. Kramar, A. D., & González-Benito, J. Cellulose-Based Nanofibers Processing Techniques and Methods Based on Bottom-Up Approach—A Review. Polymers, 14(2), 286 (2022).
8. Gunasekhar, S., & Abu-Zahra, N. Characterization of Functionalized Polyurethane Foam for Lead Ion Removal from Water. International Journal of Polymer Science, 1, 2014.
9. Guo, X., & Wu, Y. Characterizing Molecular Structure of Water Adsorbed by Cellulose Nanofiber Film Using in situ Micro-FTIR Spectroscopy. Journal of Wood Chemistry and Technology, 37(5), 383–392 (2017).
10. Barlow, D. E., Biffinger, J. C., Cockrell-Zugell, A. L., Lo, M., Kjoller, K., Lee, W. K., Pehrsson, P. E., Crookes-Goodson, W. J., Hung, C.-S., & Russell, J. N., Jr. The importance of correcting for variable probe-sample interactions in AFM-IR spectroscopy: AFM-IR of dried bacteria on a polyurethane film. Analyst, 141(16), 5590–5598 (2016).
11. Biswas, S., & Mallik, B. Solvent-mediated dynamics and stretching profile of amide modes: QM/MM simulations of N-methylacetamide in ionic and various molecular liquids. Journal of Molecular Liquids, 317, 114202 (2020).
12. Fornaro, T., Biczysko, M., Bloino, J., & Barone, V. (2016). Reliable vibrational wavenumbers for C=O and N-H stretchings of isolated and hydrogen-bonded nucleic acid bases. Physical Chemistry Chemical Physics : PCCP, 18(12), 8479-90
13. Miao, W., Chen, H., Pan, Z., Pei, X., Li, L., Li, P., Liu, J., Zhai, J., & Pan, H. (2021). Enhancement of thermal stability of polyetherimide-based nanocomposites for applications in energy storage. Composites Science and Technology, 201, 108501.
14. Liu, J., Li, H., Chang, H., He, Y., Xu, A., & Pan, B. (2019). Structure and thermal property of intumescent char produced by flame-retardant high-impact polystyrene/expandable graphite/microencapsulated red phosphorus composite. Fire and Materials, 43, 971-980.