

ISOCYANATE-FUNCTIONALIZED CHITOSAN AS A BIO-BASED REINFORCEMENT FOR POLYUREA COMPOSITES

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In this paper, modified polyurea was obtained and characterized. Only the prepolymer part of polyurea was modified using chitosan as a bio-derived reinforcing agent. The amine part remained unchanged. The prepolymer part was modified through direct physical blending and chemical grafting of chitosan to isocyanate. The modified Part A was mixed with the same part B to produce polyurea films. The FT-IR results of the modified Part A showed carbonyl bands near 1720-1730 cm⁻¹, supporting the formation of urethane and urea linkages. Physically blended systems showed a slight decrease in thermal stability. On the other hand, chemically modified chitosan increased the main degradation temperature from 284°C to 306°C, which indicates stronger interfacial bonding. The 2 wt% functionalized composite achieved about 30% higher tensile strength and 50% higher modulus while maintaining good elongation. Overall, the results suggest that chemical incorporation of chitosan can be considered a promising route for improving the thermo-mechanical performance of polyurea using a low-cost bio-derived modifier.

Keywords: modified chitosan; hybrid composite; thermal stability.

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1. Introduction

Polyurea coatings are widely used as protective coatings, waterproofing membranes, and impact-resistant applications. They have advantages such as fast curing, chemical resistance, flexibility, and energy dissipation capacity [1-3]. In addition to these advantages, prolonged environmental exposure can limit the durability of polyurea coatings [4]. Polyurea systems also remain dependent on petroleum-derived components. To improve these aspects, researchers have studied the effects of reinforcing agents on polyureas using graphene oxide, carbon

nanotubes, nanocellulose, silica, and other inorganic fillers. The main challenge in these studies is achieving good dispersion and interfacial compatibility [1,5]. Recent studies also show that the performance of polyurea and related elastomeric composites is strongly affected by filler dispersion, interfacial compatibility, and hard/soft segment structure [3,5]. Recent work on chitosan-based nanocomposites also confirms that chemical modification is an effective way to improve compatibility between chitosan and polymer matrices [6-8]. One of the potential candidates as a reinforcing agent is chitosan, which is abundant, low-cost, and contains reactive hydroxyl and amino groups. Several studies have been conducted on polyurethane systems. Polyurethanes are chemically closest to polyurea; however, the faster isocyanate-amine reaction in polyurea creates additional challenges for the integration of chitosan into polyurea. To achieve maximum compatibility and reinforcement effect, in this study chitosan was chemically integrated into polyurea systems in a few steps.

This approach aims to clarify the reaction of chitosan with isocyanates and to compare physical blending with chemical grafting as two different routes for incorporating chitosan into polyurea. The obtained materials were evaluated in terms of chemical structure, morphology, thermal behavior, dynamic mechanical behavior, and mechanical performance [3,6,7,8-14].

2. Materials and Methods

2.1 Materials

Chitosan (CS; purity 98.1%, moisture <1.5%) was sourced as a powder from Shaanxi Tinchon Biotechnology, China. The isocyanate component was 2,4'/4,4'-diphenylmethane diisocyanate (50%/50% wt) (Ongronat 3600, BorsodChem, Hungary). Triethylamine (Et_3N , $\geq 99.5\%$, Sigma-Aldrich) served as the catalyst. DESMOPHEN 2061 BD (Bayer) was used as the polyol. The amine curatives were Jeffamine D2000 (Huntsman) and Ethacure 300 (Albemarle). Propylene carbonate was used as the solvent. Additives included BYK A 530 as a defoamer and Disperbyk 2152 as a dispersant (BYK, Germany).

2.2 Methods

The original polyurea was modified with chitosan in two ways: physically and chemically. For the chemical route, chitosan was reacted with the isocyanate component, which can react with hydroxyl and amine groups present in chitosan. The obtained intermediate was then mixed with the remaining chemicals of Part A. The final product was Part A chemically reinforced with chitosan. For the physically modified polyurea, chitosan was dispersed mechanically in Part A, prepared using the standard recipe. Part B was prepared according to the manufacturer's formula and was used without any modification. Part A and Part B

were combined in a 1:1 volumetric ratio using a double syringe equipped with a static mixer. The blank polyurea was prepared by mixing unmodified Part A with Part B under the same conditions. Three types of polyurea films were prepared. The chemically modified polyurea was obtained by mixing chitosan-reinforced Part A with Part B. The physically modified polyurea was prepared by mixing Part A containing mechanically dispersed chitosan with Part B. The blank polyurea was prepared from unmodified Part A and Part B. The resulting polyureas were cast into PTFE molds. After initial curing at room temperature for 5 min, the films were post-cured at 50 °C for 24 h and then cooled to room temperature before characterization.

Step 1. Synthesis of chitosan-isocyanate intermediate (CS-ISO)

Chitosan (2.5 g) was dispersed in toluene (50 mL) at ambient temperature. Triethylamine (6.34 g) was added to catalyze the reaction. Ongronat 3600 (15.30 g) was then added dropwise. After being stirred under a nitrogen atmosphere for 24 h, the amino and hydroxyl groups in chitosan were expected to react with isocyanate groups to form urea and urethane linkages. After vacuum filtration, the obtained yellowish solid was repeatedly washed with anhydrous toluene, thereby removing the remaining unreacted MDI and excess triethylamine catalyst. The vacuum-dried intermediate (CS-ISO, 3.9 g) was processed immediately because the material is sensitive to ambient moisture. The isolated product mass corresponds to a yield of approximately 27.6%, calculated as $(3.9 \text{ g}/14.13 \text{ g}) \times 100$ on an idealized theoretical product-mass basis. This value refers only to the recovered mass of the intermediate and not to the grafting efficiency.

Step 2: Preparation of CHITOSAN-Grafted Prepolymer (Part A)

To prepare the prepolymer, 0.5, 1.0, and 1.5 g of the CS-ISO intermediate were incorporated into Ongronat 3600 (21.50 g, 0.171 mol NCO groups) to obtain prepolymers containing 1, 2, and 3 wt% CS-ISO, respectively, and mixed for 30 min. Then, DESMOPHEN 2061 BD (25.50 g, 0.02545 mol OH groups) was added to the mixture and heated at 80 °C with vigorous stirring for 4 hours. After the system cooled to room temperature, 2.50, 2.00, and 1.50 g of propylene carbonate were added, respectively, under vacuum to obtain homogeneous liquids. The nominal NCO/OH equivalent ratio of the MDI/polyol feed was 6.71, excluding the reactive groups of CS-ISO. The theoretical residual NCO content was calculated as 12.22 wt% on the 50.0 g Part A formulation basis, using 21.50 g of MDI with 33.4 wt% NCO and 25.50 g of polyol with an OH number of 56 mg KOH g⁻¹. These calculations assume complete consumption of the polyol OH groups and exclude NCO contributions or consumption associated with CS/CS-ISO and other side reactions. The CS-ISO contents were calculated based on the total mass of Part A and adjusted to 1, 2, and 3 wt%. A second sample group containing unmodified chitosan at the same loadings was prepared by physical blending and used as a reference (Table 1).

Table 1. Nomenclature, composition of the prepared samples.

Sample code	Filler type	Filler content, %	Preparation method
PU	None	0	Neat polyurea
PU-1%CS	Unmodified Chitosan	1	Physical blending
PU-2%CS	Unmodified Chitosan	2	Physical blending
PU-3%CS	Unmodified Chitosan	3	Physical blending
PU-1%CS-ISO	Functionalized Chitosan	1	Chemical grafting
PU-2%CS-ISO	Functionalized Chitosan	2	Chemical grafting
PU-3%CS-ISO	Functionalized Chitosan	3	Chemical grafting

Step 3: Synthesis of the diamine phase (Part B)

Part B was prepared by mixing 72.3 wt% Jeffamine D2000 and 26.7 wt% ETHACURE 300. The components were stirred at ambient temperature until a uniform phase formed. BYK A 530 and Disperbyk 2152 were then added at 0.5 wt% of the total Part B composition (1.0 wt% combined). Parts A and B were mixed at a 1:1 volume ratio, corresponding to an NCO/NH equivalent ratio of 1.03, using a dual syringe system and cast directly into PTFE molds. Pure polyurea films, free of chitosan, were cast following the identical steps. The films were subsequently cured at 50 °C for 24 h and left to cool down at room temperature for characterization.

2.3 Characterization

FTIR spectra were collected on a Bruker VERTEX 70 (Bruker, Billerica, MA, USA) equipped with an ATR unit with a Ge crystal. Each spectrum was the average of 32 scans over 400–4000 cm⁻¹.

XPS was performed on a Thermo Scientific K-Alpha (East Grinstead, UK) using monochromatic Al K α radiation (1486.6 eV). The base pressure during acquisition was $\sim 2 \times 10^{-9}$ mbar. Binding energies were referenced to C 1s at 284.8 eV. Shirley background subtraction was applied before peak fitting. Survey spectra were recorded at a pass energy of 200 eV and high-resolution spectra at 20 eV.

Dynamic mechanical analysis was carried out using a TRITEC 2000 B (Triton Technology Ltd., now Mettler Toledo). Rectangular specimens were tested in single-cantilever mode at 1 Hz. Temperature was ramped from -40 to 100 °C at 5 °C min⁻¹.

Thermogravimetric analysis was run on a Netzsch TG 209 F1 Libra (Selb, Germany). Approximately 5 mg of sample in a platinum pan was heated from 20 to 800 °C at 10 °C min⁻¹ under nitrogen at 10 mL min⁻¹.

Tensile properties were measured on an Instron 3382 universal testing machine (Norwood, MA, USA) at a crosshead speed of 5 mm min⁻¹ and 45–50% relative humidity. Specimens were approximately 10 $\times$ 1 cm. At least three replicates were tested per composition, and averages are reported. Procedures followed EN ISO 527-3:2018.

Fracture-surface morphology was examined on a Hitachi TM4000plus II tabletop SEM (Spectral, Lidingo, Sweden) at 15 kV. Samples were sputter-coated with a thin gold layer to minimize charging, reduce beam damage, and improve signal quality.

3. Results and Discussion

3.1 Chitosan modification characterization

The reported XPS surface atomic fractions for CS and CS-ISO were 56.71 and 64.93 at.% C, and 43.29 and 31.66 at.% O, respectively (Table 2). The corresponding O/C ratios were 0.76 and 0.49. For CS-ISO, the reported nitrogen fraction was 3.41 at.% ($N/C = 0.053$). No quantitative nitrogen result was reported for CS in the supplied dataset; therefore, its nitrogen content cannot be treated as zero, and a change in nitrogen content or N/C ratio cannot be established. The C 1s spectral changes discussed below provide complementary evidence for surface modification.

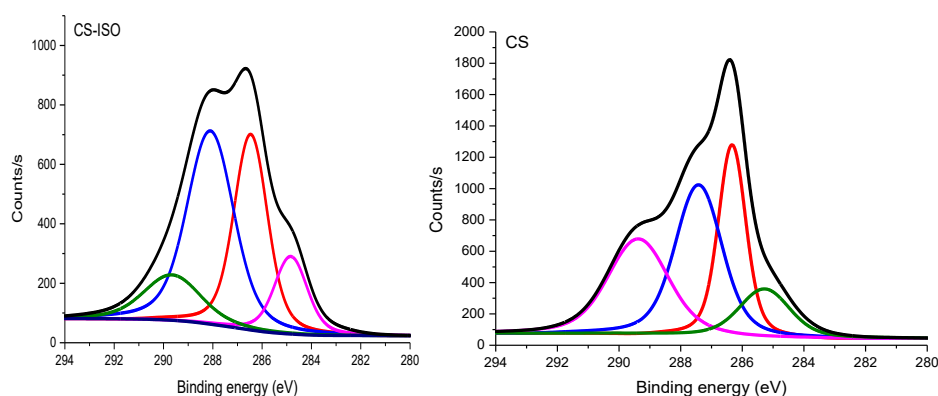


Figure 1. C1s XPS spectra of chitosan (CS) and MDI-modified chitosan (CS-ISO).

Unmodified chitosan (CS): C-C/C-H ~ 284.4 eV; C-O ~ 286.2 eV; O-C-O ~ 287.4 eV; minor acetyl ~ 289 eV. Modified chitosan (CS-ISO) shows a stronger C-C aromatic signal, a broadened signal at ~ 285 eV, and contributions from overlapping C-O/C-N signals. XPS analysis suggests chemical attachment occurs; also, owing to XPS's surface-sensitive nature, it cannot confirm chemical bonds of the entire bulk.

Table 2. Surface atomic composition (at.%) of chitosan (CS) and MDI-modified chitosan (CS-ISO) from XPS data.

Sample	C1s (%)	O1s (%)	N1s (%)
CS	56.71	43.29	-
CS-ISO	64.93	31.66	3.41

Note: "-" denotes a quantitative nitrogen result not reported in the supplied XPS dataset; it does not indicate zero nitrogen or establish that nitrogen was below the detection limit.

FT-IR spectroscopy was performed to follow the chemical bond formation reaction between chitosan and isocyanate. In Fig. 2, the spectra for pure chitosan and that modified with MDI are presented. As can be seen from the spectrum, pure chitosan shows the characteristic absorbance of -OH and -NH groups as a broad peak in the area 3200-3500 cm^{-1} , an area in which the intensity decreases significantly in the case of modified chitosan (CS-ISO). This change suggests partial consumption of hydroxyl and amine groups, consistent with the formation of urethane and urea linkages [15,16].

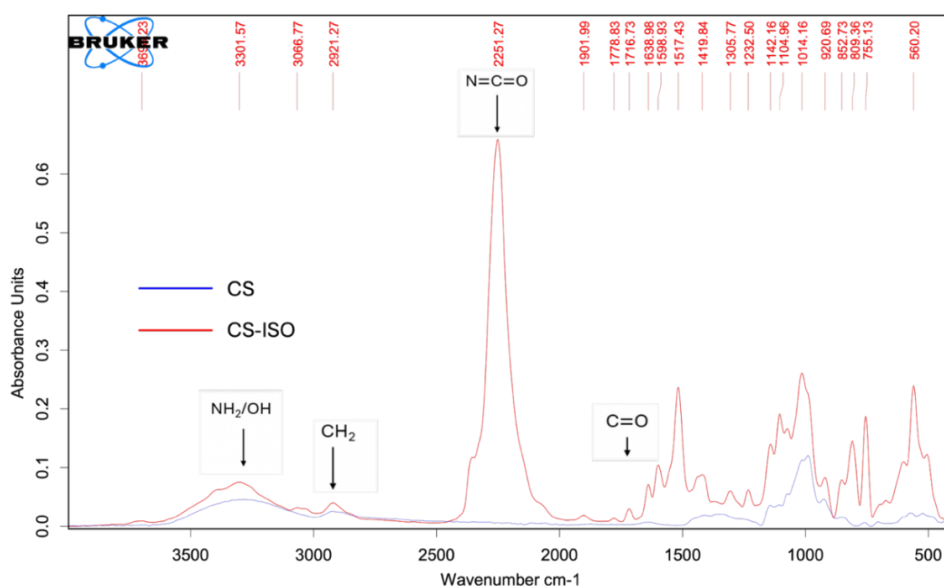


Figure 2. FT-IR spectra of CS and CS-ISO.

In addition to these signals, in the spectrum of pure chitosan, aliphatic C-H bands between 2870-2930 cm^{-1} and vibrations specific to the C-O-C bonds in the saccharide structure at 1020-1070 cm^{-1} are distinguished. The presence of weak amide I and II signals at ~ 1622 and ~ 1590 cm^{-1} is consistent with residual acetyl groups, in agreement with literature data [8]. After chitosan attachment, important changes were observed. The FT-IR spectrum of CS-ISO shows a characteristic N-H vibration at ~ 1572 cm^{-1} and a C-N stretching band at ~ 1251 cm^{-1} , supporting the formation of urea linkages [6,17]. The absorption region between 1510 and 1595 cm^{-1} becomes more intense due to the phenyl groups of the isocyanate, while the increased intensity between 1700 and 1730 cm^{-1} can be assigned to carbonyl groups (C=O) associated with urethane and urea structures. In addition, the characteristic

N=C=O band at $\sim 2250\text{ cm}^{-1}$ suggests the presence of residual unreacted NCO groups [17].

Overall, the FT-IR and XPS results support the chemical functionalization of chitosan with isocyanate-containing species. However, residual NCO content, grafting efficiency, extractable fraction, and gel fraction were not quantitatively determined; therefore, the degree of grafting should be considered a limitation of the present study.

Pure and modified chitosan were examined by TGA. The corresponding curves are shown in Fig. 3, and the thermal parameters are summarized in Table 3. Both materials display two-step degradation. In the first stage, a small mass loss was observed, which is related to physically bound water

The second stage of decomposition is associated with depolymerization processes such as dehydration of saccharide units, deacetylation of residual N-acetyl groups, and cleavage of glycosidic bonds [18,19]. The modified CS-ISO sample showed a modest but consistent improvement in thermal stability. The $T_{d3\%}$ value increased from $103.1\text{ }^{\circ}\text{C}$ for CS to $119.9\text{ }^{\circ}\text{C}$ for CS-ISO, while $T_{d5\%}$ increased from $219.8\text{ }^{\circ}\text{C}$ to $226.8\text{ }^{\circ}\text{C}$. The main decomposition also shifts slightly: T_{max} rises from $312.6\text{ }^{\circ}\text{C}$ for CS to $314.4\text{ }^{\circ}\text{C}$ for CS-ISO. These small but reproducible changes are related to reduced hygroscopicity and stronger intermolecular interactions introduced by MDI segments and urea linkages.

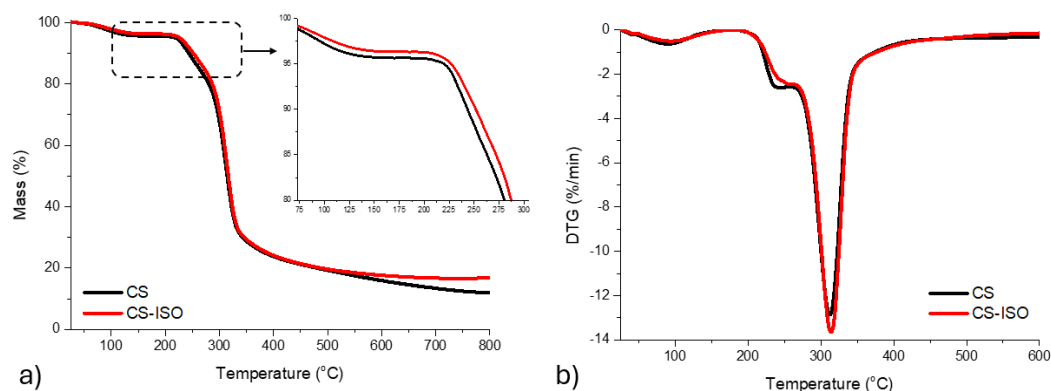


Figure 3. TGA(a) and DTG(b) curves of CS and CS-ISO.

Table 3. Thermal parameters extracted for CS and CS-ISO.

Sample	$T_{d3\%}$ ($^{\circ}\text{C}$)	$T_{d5\%}$ ($^{\circ}\text{C}$)	$T_{\text{max}1}$ ($^{\circ}\text{C}$)	$T_{\text{max}2}$ ($^{\circ}\text{C}$)	Residual mass (%)
CS	103.1	219.8	246.1	312.6	11.94
CS-ISO	119.9	226.8	247.7	314.4	16.88

Although the changes are modest, they are consistent with the improved thermal behavior observed for the CS-ISO-containing polyurea composites compared with the physically blended CS systems.

At elevated temperatures, CS-ISO leaves more residue than CS (16.88% vs 11.94%). This behavior is reasonable given the aromatic content of the MDI fragment and the propensity of urea structures to form condensed char, which can contribute to improved thermo-oxidative resistance [20,21].

3.2 Thermogravimetric analysis of PU composites

The thermal stability of neat polyurea (PU) and composites containing either unmodified chitosan (PU-x%CS, $x = 1-3$) or isocyanate-functionalized chitosan (PU-x%CS-ISO) was assessed by TGA. Representative curves are given in Figures 4 and 5, and the key parameters are summarized in Table 4. All systems show the two-step decomposition typical of aromatic polyurea: a first maximum at about 280-306 °C linked to scission of urea linkages and cleavage of soft segments, followed by a second maximum at roughly 378-387 °C associated with breakdown and partial rearrangement of the aromatic hard domains [22].

At 1-2 wt% CS, the initial degradation temperatures drop slightly. This likely reflects the hydrophilic character of chitosan, where residual amine sites and absorbed water can promote early urea dissociation. Consistently, $T_{\max,1}$ remains nearly unchanged at low loading and shifts upward only at 3 wt% CS. Char residue decreases monotonically with CS addition, consistent with dilution of the aromatic hard phase and the readier volatilization of the polysaccharide domains. These results suggest that, without chemical grafting, unmodified CS acts mainly as a less thermally stable dispersed phase within the PU matrix.

3.2.1 PU-CS-ISO series

A different pattern emerges when CS is functionalized. Increasing CS-ISO content raises the early degradation temperatures and produces a clear rise in $T_{\max,1}$, reaching 306 °C at 2-3 wt% loading; $T_{\max,2}$ also shifts slightly upward.

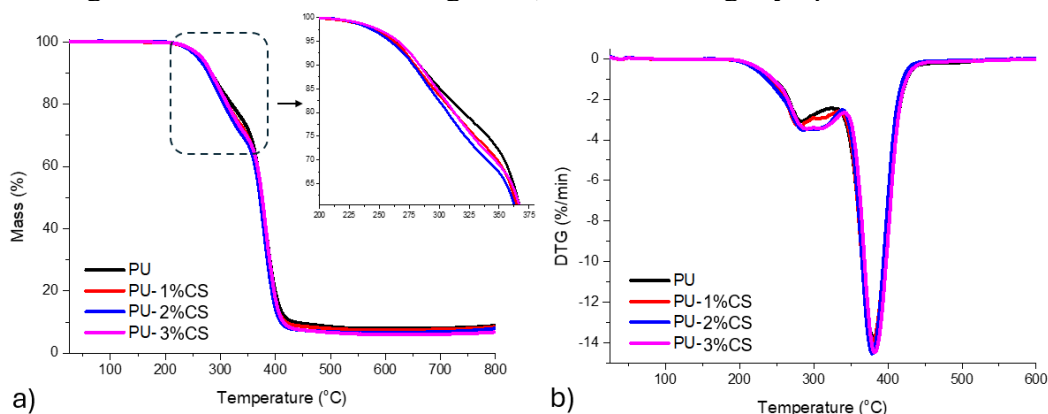


Figure 4. TGA and DTG of PU nanocomposite samples based on CS.

These changes suggest better compatibility, probably due to possible covalent interactions between residual isocyanate groups on CS-ISO and the matrix, reduced chain mobility, and the stabilizing effect of aromatic MDI fragments [17,20,21,23].

Table 4. Thermal stability parameters for PU and CS-based nanocomposites.

Sample	T _{d3%} (°C)	T _{d5%} (°C)	T _{max1} (°C)	T _{max2} (°C)	Residual mass (%)
PU	251.9	264.5	283.8	380.4	8.87
PU-1%CS	249.3	262.3	282.6	379.7	8.54
PU-2%CS	247.4	259.2	283.5	378.3	8.02
PU-3%CS	253.2	265.9	290.4	382.2	6.81
PU-1%CS-ISO	249.3	264.7	289.4	382.2	4.68
PU-2%CS-ISO	253.4	267.3	306.0	384.3	6.38
PU-3%CS-ISO	256.9	270.2	306.0	386.7	6.76

Therefore, the improved thermal stability of the CS-ISO composites should be interpreted mainly as a delay in matrix degradation rather than as an increase in char-forming ability.

3.2.2 Char formation

In the CS-ISO series, the residue decreased from 8.87% for neat PU to 4.68% at 1 wt% CS-ISO, then increased to 6.38% and 6.76% at 2 and 3 wt% CS-ISO, respectively. These values remained below that of neat PU, indicating that the improved thermal stability reflects delayed degradation rather than increased char formation. The observed trend suggests that CS-ISO affects the degradation pathway and improves the resistance of the matrix to thermal decomposition, although the final char formation capacity remains lower than that of pure PU.

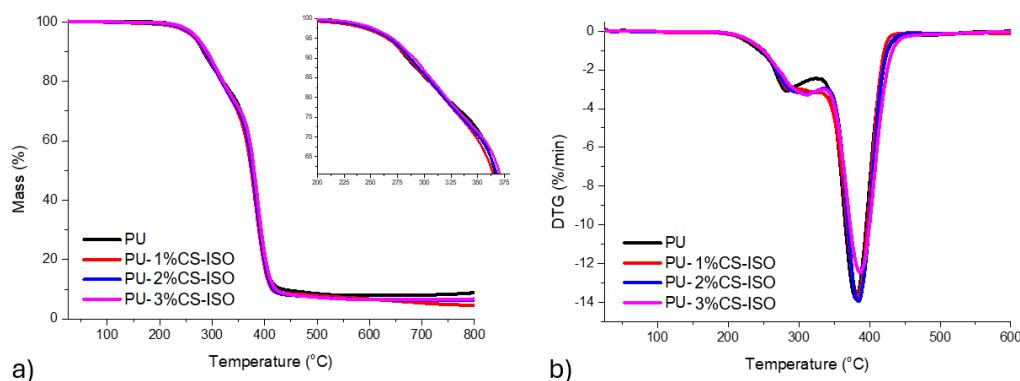


Figure 5. TGA and DTG of PU nanocomposite samples based on CS-ISO.

3.3 Dynamic mechanical analysis (DMA)

The viscoelastic behavior of neat PU and the composites was evaluated by DMA. Temperature-dependent storage modulus (E') and Tan Delta are shown in Fig. 6.

The storage modulus (E') was strongly affected by the type of filler. PU showed a typical rubbery plateau. The incorporation of untreated chitosan did not provide a consistent reinforcement effect, especially at higher loading. This behavior may be related to limited dispersion, particle aggregation, and weak interfacial contact, which reduce stress transfer between the matrix and the filler [24-26]. In contrast, the PU-CS-ISO composites showed higher E' over the rubbery temperature range. This behavior may be related to stronger interactions between the functionalized chitosan and the polyurea matrix, which may restrict segmental mobility and improve stress transfer [27].

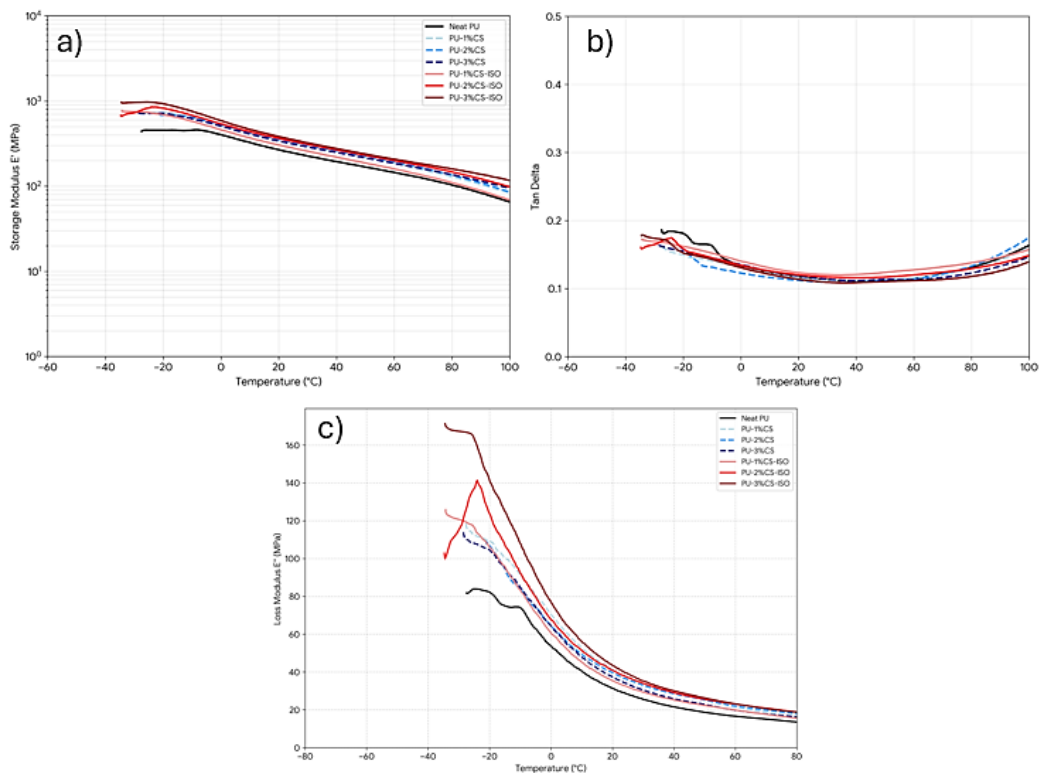


Figure 6. a) Storage modulus of polyurea nanocomposite systems; b) Tan Delta of polyurea nanocomposite systems; c) Loss modulus of polyurea nanocomposite systems.

The T_g values were evaluated from the loss modulus peak. PU showed a T_g of -25.4 °C, while PU-3%CS-ISO showed a lower T_g of -32.5 °C. Normally, the addition of rigid fillers can increase T_g by restricting chain movements. We show here a counterintuitive phenomenon in PU - CS - ISO. The decrease in T_g upon incorporating functionalized fillers may be related to changes in the local hydrogen-bonding network of the polyurea matrix. Such changes in local bonding may increase the free volume around amorphous polymer segments, particularly near the interfaces between hard and soft segments. In other words, the functionalized

chitosan does not just act as rigid fillers but also may modify chain relaxation by changing localized hydrogen-bonding interactions, which may contribute to the observed changes in the DMA response.

A significant improvement was observed in the loss modulus (E''), which represents the energy dissipation capacity of the material. The pure polyurea exhibited a peak in the loss modulus of 83 MPa. The incorporation of unmodified chitosan resulted in minimal changes. This may be related to weak interaction between free chitosan particles and the polyurea matrix. However, the PU-3%CS-ISO reached a peak E'' of 171 MPa. This means a remarkable 106% increase compared to the unmodified polyurea. This enhancement may be attributed to two possible mechanisms. First, possible covalent interactions and the increased surface roughness observed in SEM may increase internal friction during dynamic loading.

Second, the SEM micrographs suggest that well-dispersed CS-ISO particles may promote localized plastic deformation and crack deviation in the polymer matrix. These processes may contribute to higher viscous energy dissipation before failure. Therefore, these explanations should be considered plausible mechanisms based on DMA and morphology results, rather than direct proof of a specific molecular rearrangement.

3.4 Mechanical analysis

The tensile properties of neat PU and chitosan-modified polyurea composites are summarized in Table 5. The values are reported as average values from three specimens.

Table 5. Summary of mechanical properties.

Sample	Tensile strength (MPa)	Young's modulus (MPa)	n
PU	2.32	22.3	3
PU-1%CS	1.83	18.0	3
PU-2%CS	2.40	24.0	3
PU-3%CS	2.95	28.1	3
PU-1%CS-ISO	2.80	29.1	3
PU-2%CS-ISO	3.05	31.7	3
PU-3%CS-ISO	3.02	33.2	3

As shown in Table 5, the neat polyurea exhibited a tensile strength of 2.32 MPa. This value is consistent with the commercial formulation used in this study, which is designed as a semi-structural joint filler rather than a high-elasticity polyurea. With the addition of 1 wt% unmodified chitosan, the tensile strength decreased to 1.83 MPa, which may be attributed to poor interfacial adhesion and particle agglomeration. Similar behavior has been reported in the literature [28,29]. In contrast, 1 wt% chemically grafted chitosan (PU-1%CS-ISO) resulted in a higher tensile strength of 2.80 MPa, suggesting improved interfacial bonding and load transfer.

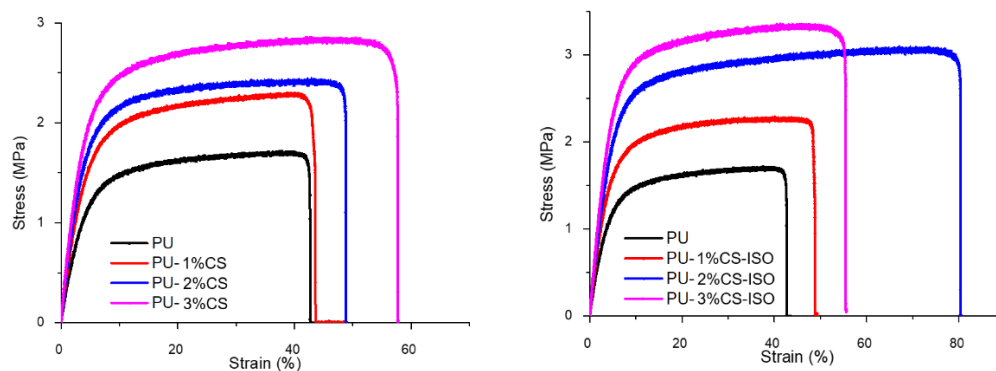


Figure 7a. Stress-strain curves of neat and modified polyureas.

Most composite systems showed a higher Young's modulus than PU, except PU-1%CS. The extent of reinforcement depended on the type of chitosan incorporation and the filler loading. In the case of physical mixtures (PU-CS), the increase in stiffness was limited to +26% for a concentration of 3% wt., reflecting a low compatibility at the interface. In contrast, the PU-CS-ISO series showed a substantial jump, reaching 33.2 MPa (i.e. +49% compared to pure polyurea) at the same load level. This mechanical superiority comes from the formation of urethane and urea bonds on the chitosan surface, confirmed by specific bands in the FTIR spectra.

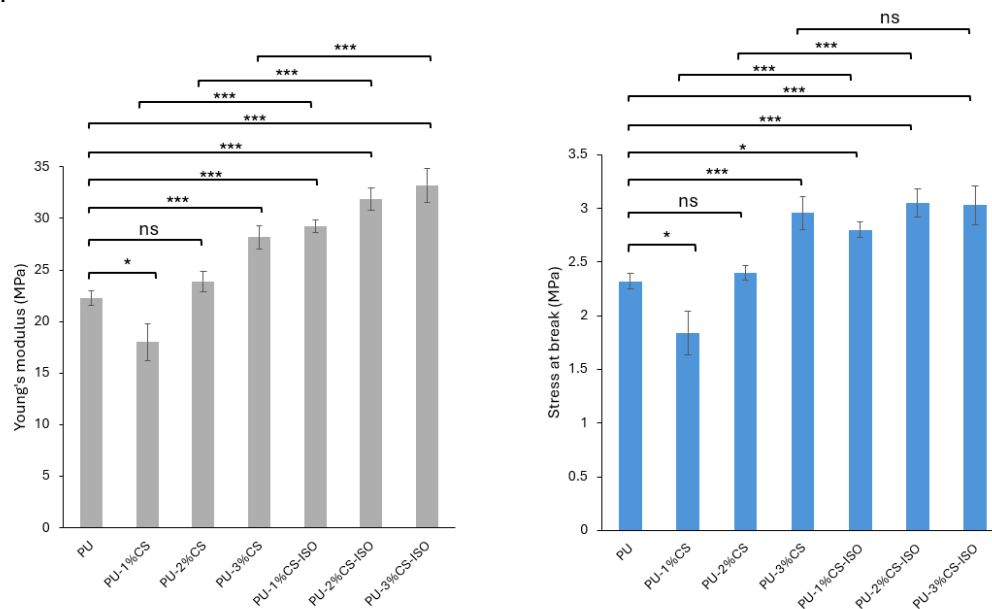


Figure 7b. Mechanical performance of neat and chitosan-modified polyureas.

3.4.1 Ductility and Chemical Interface Analysis

In the case of composites with physically incorporated chitosan (PU-CS series), the elongation at break decreases steadily with increasing chitosan content. In contrast, the PU-CS-ISO series follows a different trend, where the composite with 2% CS-ISO reaches a maximum of 73.25% (+34% compared to the control).

This specific behavior, in particular the difference between the 2% and 3% concentration, may reflect the balance between reinforcement and mobility (2% CS-ISO). Although both composites, the one with 2% and 3%, present the same chemical bonds between isocyanates and chitosan, a more favorable distribution at 2% may allow for efficient stress transfer while leaving enough space between the particles for the polymer chains to move and reorganize under stress.

Furthermore, an over-restriction phenomenon (3% CS-ISO) was noticed. In the case of composites with 3%, the density of grafting points and the proximity of chitosan particles excessively block the movement of the chains (over-restriction). At the same time, direct contacts between chitosan particles (filler-filler contacts) can occur, which act as points of embrittlement. The result is an increase in stiffness (maximum Young's modulus), but at the cost of a sudden decrease in elongation at break to 35%.

Nonetheless, the fracture morphology is visible in the SEM images (Fig. 8). At 2%, the fracture surface is rough and shows a "tortuous path", a sign that the matrix has consumed a lot of energy to deform plastically. In physical mixtures or at concentrations as high as 3%, chitosan blocks the movement of the polymer chains instead of supporting them. Because of this, the bond between the components is no longer effective. The result is a stiff material that breaks much more quickly.

3.5 Morphological characterization

The fracture surface morphologies of PU and the modified composites were examined by SEM to visualize the dispersion state and failure mechanisms. SEM micrographs of fracture surfaces are shown in Fig. 8 for neat PU and for composites with CS or CS-ISO. The observations were further quantified using ImageJ software to measure the area of the surface features.

The neat PU fracture surface appeared relatively smooth, which is consistent with a more homogeneous polymer structure and limited phase separation. Unlike pure polyurea, the morphology of the physical blends (PU-CS series) is dominated by flake-like structures. These suggest that, in the absence of a chemical bond, chitosan does not fully integrate into the polymer network, remaining as distinct domains in the matrix [6]. Quantitative analysis shows that the average surface area of these structures increases significantly with the addition of chitosan content. The value increases from 13551 nm² for the sample with 1% CS, reaching 21158 nm² for the 3% CS concentration.

Table 6. Flake-like structures area calculated from SEM images.

Sample	Average flake-like structures area, nm ²
PU-1%CS	13551
PU-2%CS	19932
PU-3%CS	21158

This increase in the size of the flake-like structures confirms the tendency of chitosan particles to agglomerate at higher concentrations. The results suggest limited compatibility in the case of the physical blend, thus highlighting the need for chemical functionalization (such as CS-ISO) to obtain a finer dispersion and a more homogeneous structure.

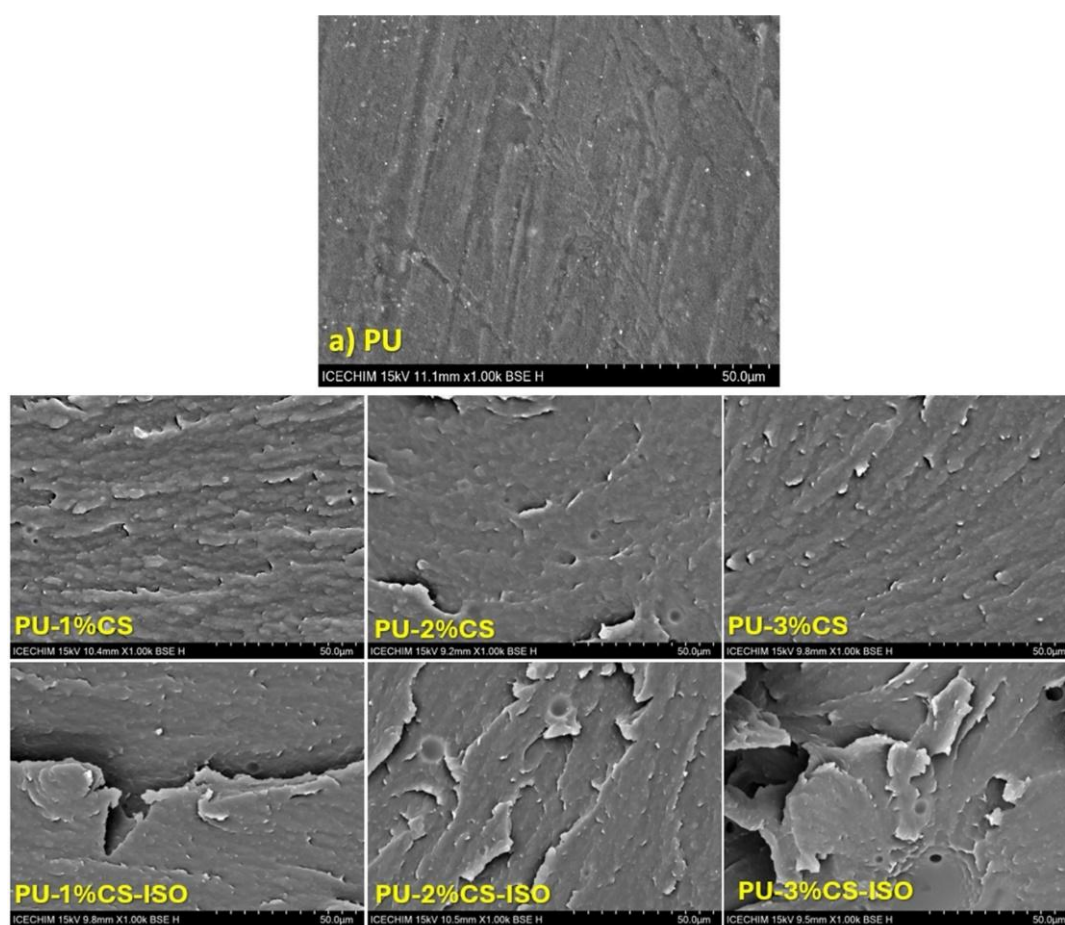


Figure 8. SEM micrographs of fracture surfaces of neat PU and chitosan-modified PU composites prepared by physical blending (PU-CS) and chemical functionalization (PU-CS-ISO).

In direct contrast to the physical blends, the chemically modified series (PU-CS-ISO) presents a quite different morphology, characterized by a rough fracture surface and a tortuous path. This change suggests better integration of the modified

chitosan into the polymer network and a reduced tendency for particle detachment or agglomeration.

The irregular surface suggests that the matrix may promote matrix deformation and shearing processes (tearing) before rupture. A stronger interfacial interaction may contribute to improved resistance to crack propagation and may support the proposed reinforcement mechanism. This morphology is also consistent with the higher loss modulus observed for the CS-ISO composites.

In conclusion, the SEM results support the mechanical findings: simple blending of CS yields local defects and mechanically weak materials, while chemical functionalization (CS-ISO) improves dispersion and adhesion.

4. Conclusions

Functionalization of chitosan with MDI improved its compatibility with the polyurea matrix. The formation of urethane and urea linkages was supported by FT-IR and XPS results. For the chitosan powders, CS-ISO showed only a slight shift to higher degradation temperatures and a higher residue compared with unmodified chitosan. However, the effect became more relevant after incorporation into the PU matrix. When unmodified chitosan was physically blended into PU, the improvements in stiffness and strength were not consistent. Thus, this behavior indicated limited interfacial adhesion and local aggregate formation, whereas for MDI-modified chitosan, the mechanical property increase was observed differently, with a regular, simultaneous increase of tensile strength, Young's modulus, and elongation at break reported at 2 wt% CS-ISO, indicating a better balance between stiffness and strength. The SEM observations supported it, as shown by a clearer interface and more ductile fracture morphology for the CS-ISO composites.

The TGA results also showed different behavior for the two modification routes. Unmodified chitosan caused an early decrease in thermal stability and reduced the final residue. In contrast, CS-ISO reduced this destabilizing effect and, at higher loadings of 2 wt% and above, shifted the main degradation temperatures upwards. Hence, CS-ISO was found to act as a more effective reinforcement in PU systems that need to be subjected to thermal treatments compared to plain physical dispersion of chitosan.

Results outline a practical route for tuning polyurea with a bio-sourced filler while keeping the processing relatively simple. Protective coatings and structural materials can be considered promising future directions. However, these applications have not yet been fully demonstrated and should be confirmed by application-specific tests. These aspects could include durability, adhesion, impact resistance, and aging performance. Future work should also quantify the interfacial chemistry.

Author Contributions

Conceptualization, K.D. and H.I.; methodology, K.D., M.I.N., C.D., and A.L.; investigation, K.D., M.I.N., C.D., and A.L.; formal analysis, K.D. and H.I.; writing - original draft preparation, K.D.; writing - review and editing, all authors; supervision, H.I.

Data Availability Statement

Data supporting the findings of this study are available upon reasonable request from the corresponding author.

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Conflicts of Interest

The authors declare no conflict of interest.

Artificial Intelligence Disclosure

No artificial intelligence-based or generative tools were used in the preparation of this manuscript.

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REFERENCES

- [1] Zhao, K.; Gong, X.; Zhang, C.; Dai, J.; Meng, Q. Advancements in polyurea-based nanocomposites: Properties, applications and challenges. *Advanced Nanocomposites* **2025**, *2*, 258-287. DOI: 10.1016/j.adna.2025.04.001.
- [2] Wu, J.; Wang, P.; Tian, Y.; Liang, S.; Zhang, W.; He, X.; Li, Q.; Du, J. Self-healing superhydrophilic polyurea composite coating for durable oil/water separation. *Surf. Coat. Technol.* **2025**, *512*, 132416. DOI: 10.1016/j.surfcoat.2025.132416.
- [3] Wang, Y.; Ding, L.; Lin, J.; Qiu, X.; Wu, C.; Liu, C.; Tian, Y.; Zhang, R.; Huang, W.; Ma, M. Recent developments in polyurea research for enhanced impact penetration resistance and blast mitigation. *Polymers* **2024**, *16*, 440. DOI: 10.3390/polym16030440.
- [4] Peng, C.; Ren, J.; Wang, Y. Degradation behavior and lifetime prediction of polyurea anti-seepage coating for concrete lining in water conveyance tunnels. *Materials* **2024**, *17*, 1782. DOI: 10.3390/ma17081782.
- [5] Toader, G.; Diacon, A.; Axinte, S. M.; Mocanu, A.; Rusen, E. State-of-the-art polyurea coatings: Synthesis aspects, structure-properties relationship, and nanocomposites for ballistic protection applications. *Polymers* **2024**, *16*, 454. DOI: 10.3390/polym16040454.
- [6] Piotrowska-Kirschling, A.; Brzeska, J. The effect of chitosan on the chemical structure, morphology, and selected properties of polyurethane/chitosan composites. *Polymers* **2020**, *12*, 1205. DOI: 10.3390/polym12051205.
- [7] Shih, Y.-F.; Lin, S.-H.; Xu, J.; Su, C.-J.; Huang, C.-F.; Hsu, S.-H. Stretchable and

- biodegradable chitosan-polyurethane-cellulose nanofiber composites as anisotropic materials. *Int. J. Biol. Macromol.* **2023**, *230*, 123116. DOI: 10.1016/j.ijbiomac.2022.123116.
- [8] Wei, C.-T.; You, J.-L.; Chin, K.-Y.; Chang, S.-M.; Jian, S.-Y.; Cheng, A.-Y. Synthesis and characterization of eco-friendly chitosan-based waterborne polyurethanes and their ultraviolet degradation properties. *Polym. Degrad. Stab.* **2025**, *233*, 111169. DOI: 10.1016/j.polymdegradstab.2024.111169.
- [9] Cui, X.; Guo, M.; Han, S.; Li, S.; Yu, Y.; Zhang, Y.; Meng, Q. Flexible and high-strength porous graphene/polyurea composite film for multifunctional applications. *Coatings* **2024**, *14*, 1098. DOI: 10.3390/coatings14091098.
- [10] Santamaria-Echart, A.; Fernandes, I.; Barreiro, F.; Corcuera, M. A.; Eceiza, A. Advances in waterborne polyurethane and polyurethane-urea dispersions and their eco-friendly derivatives: A review. *Polymers* **2021**, *13*, 409. DOI: 10.3390/polym13030409.
- [11] Necolau, M. I.; Damian, C. M.; Fierăscu, R. C.; Chiriac, A. L.; Vlăsceanu, G. M.; Vasile, E.; Iovu, H. Layered clay-graphene oxide nanohybrids for the reinforcement and fire-retardant properties of polyurea matrix. *Polymers* **2022**, *14*, 66. DOI: 10.3390/polym14010066.
- [12] Duman, K.; Necolau, M. I.; Bîru, E. I.; Zaharia, A.; Iovu, H. Reactive nanofiller reinforced hybrid polyurea: The role of CNC in material preparation and characterization. *Polymers* **2025**, *17*, 1527. DOI: 10.3390/polym17111527.
- [13] Sun, N.; Wang, Z.; Xu, Y.; Cong, J.; Li, J.; Bai, L.; Huo, P.; Li, Z.; Liu, Y. Synthesis of cellulose nanofiber/polysiloxane-polyurea composite materials with self-healing and reprocessing properties. *Int. J. Biol. Macromol.* **2023**, *227*, 203-213. DOI: 10.1016/j.ijbiomac.2022.12.168.
- [14] Yang, K.; Wang, S.; Chen, Y.; Dong, H.; Wang, Q.; Cheng, Q. Dynamic mechanical properties and energy absorption capabilities of polyureas through experiments and molecular dynamic simulation. *Polymers* **2025**, *17*, 107. DOI: 10.3390/polym17010107.
- [15] Sánchez-Machado, D. I.; López-Cervantes, J.; Escárcega-Galaz, A. A.; Campas-Baypoli, O. N.; Martínez-Ibarra, D. M.; Rascón-León, S. Measurement of the degree of deacetylation in chitosan films by FTIR, ¹H NMR and UV spectrophotometry. *MethodsX* **2024**, *12*, 102583. DOI: 10.1016/j.mex.2024.102583.
- [16] Varma, R.; Vasudevan, S. Extraction, characterization, and antimicrobial activity of chitosan from horse mussel *Modiolus modiolus*. *ACS Omega* **2020**, *5*, 20224-20230. DOI: 10.1021/acsomega.0c01903.
- [17] Gallego, R.; Arteaga, J. F.; Valencia, C.; Franco, J. M. Isocyanate-functionalized chitin and chitosan as gelling agents of castor oil. *Molecules* **2013**, *18*, 6532-6549. DOI: 10.3390/molecules18066532.
- [18] Kumar, S.; Koh, J. Physiochemical, optical and biological activity of chitosan-chromone derivative for biomedical applications. *Int. J. Mol. Sci.* **2012**, *13*, 6102-6116. DOI: 10.3390/ijms13056102.
- [19] Corazzari, I.; Nisticò, R.; Turci, F.; Faga, M. G.; Franzoso, F.; Tabasso, S.; Magnacca, G. Advanced physico-chemical characterization of chitosan by means of TGA coupled on-line with FTIR and GCMS: Thermal degradation and water adsorption capacity. *Polym. Degrad. Stab.* **2015**, *112*, 1-9. DOI: 10.1016/j.polymdegradstab.2014.12.006.
- [20] Celebi, H.; Ilgar, M.; Seyhan, A. T. Evaluation of the effect of isocyanate modification on the thermal and rheological properties of poly(ϵ -caprolactone)/cellulose composites. *Polym. Bull.* **2022**, *79*, 4941-4955. DOI: 10.1007/s00289-021-03753-3.
- [21] Javaid, M. A.; Waqar, M.; Ayub, M. A.; Alanazi, Y. M.; Shoaib, M.; Tanveer, Z.; Ahmad, S.; Li, D.-Q.; Ummer, K.; Hussain, M. T. Use of carboxymethyl cellulose in polyurethane synthesis for thermal applications. *Int. J. Biol. Macromol.* **2025**, *288*, 138298. DOI: 10.1016/j.ijbiomac.2024.138298.
- [22] Awad, W. H.; Wilkie, C. A. Investigation of the thermal degradation of polyurea: The effect

- of ammonium polyphosphate and expandable graphite. *Polymer* **2010**, *51*, 2277-2285. DOI: 10.1016/j.polymer.2010.03.033.
- [23] Liu, S.-H.; Kuan, C.-F.; Ke, C.; Shen, M.; Chiang, C.-L. A novel effective halogen-free biomass-based chitosan derived flame retardant through microencapsulation technology for improved flame retardancy, thermal stability of polyurethane. *Polym. Degrad. Stab.* **2024**, *219*, 110604. DOI: 10.1016/j.polymdegradstab.2023.110604.
- [24] Jayanarayanan, K.; Rasana, N.; Mishra, R. K. Dynamic mechanical thermal analysis of polymer nanocomposites. In *Thermal and Rheological Measurement Techniques for Nanomaterials Characterization*; Thomas, S.; Thomas, R.; Zachariah, A. K.; Mishra, R. K., Eds.; Elsevier: Amsterdam, The Netherlands, 2017; pp. 123-157. DOI: 10.1016/b978-0-323-46139-9.00006-2.
- [25] Reinecker, M.; Fuith, A.; Soprunyuk, V.; Sánchez-Ferrer, A.; Mrzel, A.; Torre, R.; Schranz, W. Influence of inorganic nanoparticles on the glass transitions of polyurea elastomers. *Phys. Status Solidi A* **2013**, *210*, 2320-2327. DOI: 10.1002/pssa.201329317.
- [26] Tzelepis, D. A.; Khoshnevis, A.; Zayernouri, M.; Ginzburg, V. V. Polyurea-graphene nanocomposites-The influence of hard-segment content and nanoparticle loading on mechanical properties. *Polymers* **2023**, *15*, 4434. DOI: 10.3390/polym15224434.
- [27] Bashir, M. A. Use of dynamic mechanical analysis (DMA) for characterizing interfacial interactions in filled polymers. *Solids* **2021**, *2*, 108-120. DOI: 10.3390/solids2010006.
- [28] Qian, X.; Song, L.; Tai, Q.; Hu, Y.; Yuen, R. K. K. Graphite oxide/polyurea and graphene/polyurea nanocomposites: A comparative investigation on properties reinforcements and mechanism. *Compos. Sci. Technol.* **2013**, *74*, 228-234. DOI: 10.1016/j.compscitech.2012.11.018.
- [29] Khankhuan, A.; Morimura, Y.; Ajiro, H. Improving the mechanical properties of chitosan through blending with poly(trimethylene carbonate) copolymer. *Int. J. Biol. Macromol.* **2024**, *283*, 137830. DOI: 10.1016/j.ijbiomac.2024.137830.