Innovative: International Multi-disciplinary Journal of Applied Technology
(ISSN 2995-486X) VOLUME 03 ISSUE 07, 2025

EFFECT OF 1,4-BUTANEDIOL CHAIN EXTENDER ON THE REACTION MECHANISM OF POLYURETHANE FORMATION

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Abstract:
This study investigates the polymerization mechanism of 1,4-butanediol, used as a chain extender in the synthesis of polyurethane based on 4,4′-methylenediphenyl diisocyanate (4,4′-MDI), as well as the effect of the diisocyanate concentration on the macromolecular structure and physicomechanical properties of the polymer. During the reaction, the hydroxyl (–OH) groups of 1,4-butanediol react with the isocyanate (–NCO) groups of 4,4′-MDI to form urethane (–NHCOO–) linkages, resulting in polymer chain extension, an increase in the content of hard segments, and improved phase organization of the polymer structure. The effects of 1,4-butanediol (3–8 wt%) and 4,4′-MDI (60–75 wt%) on the polymerization kinetics, macromolecular chain growth, and crosslink density were systematically evaluated. The results demonstrated that compositions containing 4–6 wt% 1,4-butanediol and 68–70 wt% 4,4′-MDI promoted the formation of a homogeneous polyurethane macromolecular structure, providing high mechanical strength, optimum elasticity, and excellent thermal stability. Deviations from these composition ranges resulted in an increased content of residual isocyanate (–NCO) groups, non-uniform formation of the three-dimensional polymer network, and increased brittleness of the material. These findings demonstrate that optimizing the contents of the chain extender and diisocyanate is an effective approach for controlling the molecular architecture and enhancing the performance characteristics of polyurethane materials.

Keywords: Smart Grids, Artificial Intelligence, Renewable Energy Integration, Optimization Techniques, Distributed Generation

Introduction

Polyurethanes are among the most widely used classes of synthetic polymers owing to the versatility of their molecular architecture and the possibility of tailoring their properties during synthesis. The broad range of applications of polyurethane materials is primarily attributed to the ability to regulate their molecular structure by varying the type and concentration of polyols, diisocyanates, chain extenders, and branching agents. These components play a decisive role in determining the final physicochemical and mechanical properties of the polymer. Polyurethanes based on 4,4′-MDI belong to the class of aromatic diisocyanates and are characterized by high chemical reactivity, the formation of stable urethane linkages, and the development of rigid hard segments within the polymer network. The isocyanate (–NCO) groups of 4,4′-MDI readily react with hydroxyl groups of polyols and low-molecular-weight diols, leading to the formation of polyurethane macromolecules. In polyurethane synthesis, chain extenders play a crucial role in controlling the molecular architecture and phase

morphology of the resulting polymer. Among the most widely used chain extenders is 1,4-butanediol, whose two terminal hydroxyl groups react with isocyanate groups to form urethane bonds, thereby promoting the formation of hard segments within the polymer structure [1]. As a consequence, the polymer chains are extended, the molecular weight increases, and phase separation between the hard and soft segments becomes more pronounced, resulting in improved tensile strength, elasticity, and thermal resistance of the material. However, an excessive concentration of chain extender may increase the brittleness of the polymer, reduce its molecular weight, and consequently deteriorate its mechanical performance. Polyurethane synthesis was carried out via a two-step prepolymer method. In the first stage, the polyol was dehydrated under vacuum at 100–110 °C for 1.5–2 h. Subsequently, a calculated amount of 4,4′-MDI was added to the dehydrated polyol, and the reaction mixture was mechanically stirred at 75–85 °C for 20–30 min to obtain an isocyanate-terminated prepolymer [2]. In the second stage, predetermined amounts of 1,4-butanediol and a branched oligomer were introduced into the prepolymer composition. The reaction mixture was stirred at 800–1200 rpm for 3–5 min, after which it was heated to 60–70 °C, poured into preheated metal molds, and cured at 80–100 °C for 10–12 h. The cured specimens were subsequently conditioned at room temperature for 24–48 h before characterization. Experimental investigations demonstrated that systematic variation of the concentrations of 1,4-butanediol and the branched oligomer significantly affected both the polymerization process and the physicomechanical properties of the resulting polyurethane. Furthermore, molecular modeling and structural analysis using advanced computational tools, including the UCSF ChimeraX software package, revealed that increasing the chain extender content enhances hydrogen bonding between urethane groups and strengthens interphase interactions within the segmented polyurethane structure [3].

Materials and Methods

The study employed 1,4-butanediol ($C_4H_{10}O_2$, molecular weight: 90.12 g·mol^{-1}, purity: 99.5%) as the chain extender and 4,4′-methylenediphenyl diisocyanate (4,4′-MDI; $C_{15}H_{10}N_2O_2$, molecular weight: 250.25 g·mol^{-1}, NCO content: 33.4–33.8%) as the diisocyanate component. The spatial configuration and reactivity of the two hydroxyl (–OH) groups in the 1,4-butanediol molecule were investigated using three-dimensional molecular modeling to elucidate the polyurethane chain-extension mechanism. During polymerization, the hydroxyl (–OH) groups of 1,4-butanediol underwent polycondensation with the isocyanate (–NCO) groups of 4,4′-methylenediphenyl diisocyanate at 60–75 °C. The reaction mixture was stirred at 300–500 rpm for 20–30 min to ensure homogeneous mixing and complete interaction of the reactive components. In the experimental series, the concentration of 1,4-butanediol was varied from 3 to 8 wt.%, whereas the content of 4,4′-MDI ranged from 60 to 75 wt.%. For each formulation, the polymerization kinetics, crosslink density, and evolution of the macromolecular structure were systematically investigated. Upon completion of the polymerization process, the specimens were cured in a laboratory oven at 80–100 °C for 10–12 h [4]. The urethane linkages formed in the synthesized polyurethane samples were further analyzed using the UCSF ChimeraX molecular visualization and modeling software to identify residual –NCO groups and to confirm the formation of urethane carbonyl functional groups (–NHCOO–) within the polymer network. The experimental results demonstrated that a homogeneous polyurethane macromolecular structure, a high degree of crosslinking, and superior mechanical performance were achieved when the formulation contained 4–6 % 1,4-butanediol and 68–70 % 4,4′-MDI. This composition provided optimal polymer chain growth while minimizing the concentration of residual isocyanate groups, thereby promoting the formation of a more uniform and structurally stable polyurethane network. In this study, 4,4′-MDI was employed as the aromatic diisocyanate component, polyether polyol was used as the soft-segment-forming component, 1,4-butanediol (BDO) served as the chain extender, and a branched oligomer was introduced as the branching agent to promote the formation of a three-dimensional crosslinked network. All reagents used in the investigation were industrial-grade materials with a chemical purity of not less than 99%. Three-Dimensional Molecular Structure Analysis: The spatial structure of the polyurethane macromolecules and the influence of the chain extender and branched oligomer on the molecular configuration were investigated using UCSF

ChimeraX software based on three-dimensional (3D) molecular modeling. Initially, molecular models of 4,4′-MDI, 1,4-butanediol, and the branched oligomer were generated, after which polyurethane fragments formed through their mutual reactions were constructed and optimized. The resulting molecular models were visualized in UCSF ChimeraX, enabling a detailed analysis of the spatial arrangement of the macromolecular chains, urethane bond formation, intermolecular chain proximity, and the three-dimensional configurations arising from branching reactions [5]. Based on the generated 3D molecular models, the effect of 1,4-butanediol as a chain extender on macromolecular chain length and hard-segment formation was evaluated. In addition, the influence of the branched oligomer on the development of the three-dimensional polymer network and the density of intermolecular interactions was systematically assessed. The molecular visualization results served as the basis for comparing the spatial structures of polyurethane compositions with different formulations, identifying variations in chain organization, and interpreting the structural factors governing the mechanical performance of the synthesized polyurethane materials. All experimental data are presented as the mean ± standard deviation (Mean ± SD). Statistical calculations and graphical data processing were performed using Microsoft Excel and OriginPro software.

Results and Discussion

The experimental results demonstrated that the concentration of 1,4-butanediol significantly influences the reaction kinetics and molecular architecture of polyurethanes synthesized from 4,4′-MDI. During the polymerization process, the hydroxyl (–OH) groups of 1,4-butanediol react with the isocyanate (–NCO) groups of MDI to form urethane linkages (–NH–CO–O–), resulting in the progressive extension of macromolecular chains and the development of a three-dimensional polymer network. The rate of urethane bond formation was governed by the NCO/OH stoichiometric ratio, the concentration of the chain extender, and the intrinsic reactivity of the aromatic diisocyanate. The experimental investigation identified an optimum formulation containing 68–70 % 4,4′-MDI and 4–6 % 1,4-butanediol, which provided the most favorable degree of crosslinking and the most homogeneous polyurethane network structure. Under these conditions, extensive hydrogen bonding between urethane groups promoted the formation of a highly ordered segmented structure with a uniform distribution of hard domains. This structural organization contributed to enhanced mechanical strength while simultaneously preserving the elasticity and improving the thermal stability of the synthesized polyurethane. The results further indicate that the final structure and performance of the polyurethane are strongly dependent on the polymerization mechanism, particularly the NCO/OH stoichiometric ratio, the concentration of the chain extender, and the content of the aromatic diisocyanate. These parameters govern the extent of phase separation between the hard and soft segments, the crosslink density, and, consequently, the overall physic mechanical properties of the polymeric material. The optimized polyurethane composition developed in this study exhibits significant potential for the fabrication of high-strength thermosetting polyurethane materials intended for operation under severe mechanical and thermal loading conditions. The effect of varying the concentration of 1,4-butanediol on the mechanical properties of the synthesized polyurethane was systematically investigated by preparing formulations with different chain extender contents and evaluating the corresponding changes in their physicomechanical performance.

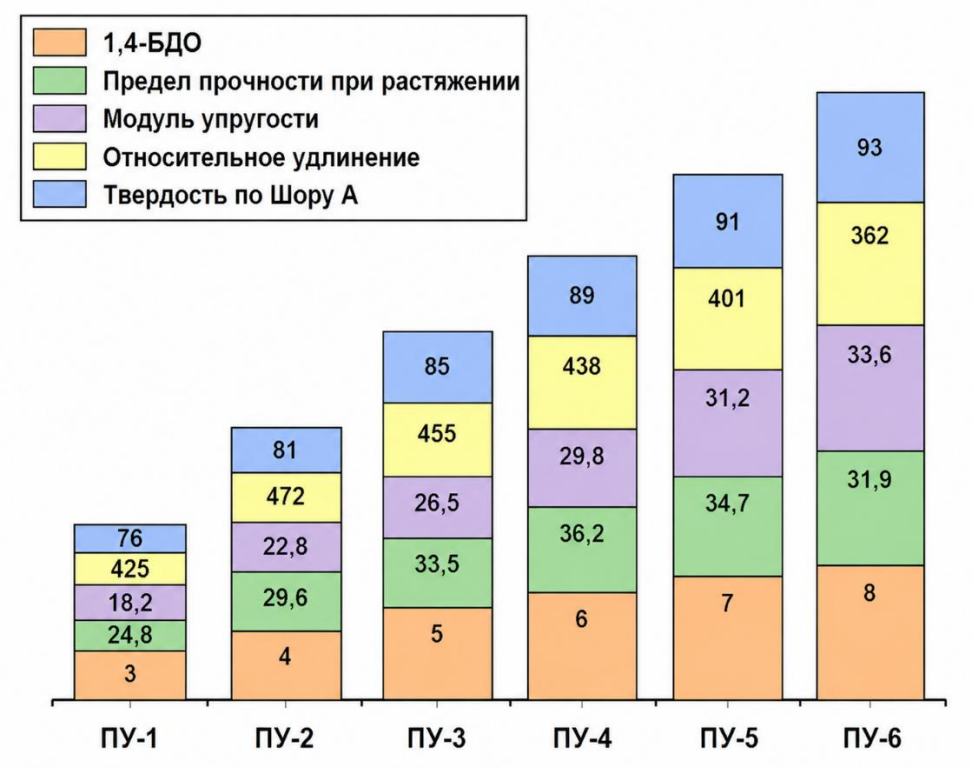

Figure 1. The amount of 1,4-butanediol polyurethanes mechanical characteristics influence

As can be seen from the data presented above, the concentration of 1,4-butanediol exerts a pronounced influence on the mechanical properties of the synthesized polyurethane. Increasing the chain extender content from 3 to 6 % resulted in a significant improvement in tensile strength, which increased from 24.8 MPa to 36.2 MPa [6]. This enhancement can be attributed to the extension of the polyurethane macromolecular chains, the increased formation of hard segments, and the more efficient development of intermolecular hydrogen bonding. A similar trend was observed for the elastic modulus, which increased from 18.2 MPa to 29.8 MPa, indicating an improvement in the material's resistance to elastic deformation. However, when the concentration of 1,4-butanediol exceeded 6%, the tensile strength began to decrease despite the continued increase in stiffness. This behavior is associated with excessive hard-segment formation, restricted mobility of the polymer chains, and the accumulation of internal stresses within the segmented polyurethane network.

Simultaneously, the elongation at break decreased from 43.8% to 36.2%, indicating that the material gradually became more rigid and lost part of its elastic deformation capability. The hardness of the polyurethane also increased with increasing chain extender concentration, rising from 76 Shore A to 93 Shore A. Based on the comprehensive evaluation of tensile strength, elasticity, and hardness, the optimum concentration of 1,4-butanediol was determined to be 5–6 %. At this composition, the synthesized polyurethane exhibited the most balanced combination of mechanical strength, flexibility, and hardness, making it a promising material for high-performance applications, including molds, structural components, and protective coating systems operating under demanding service conditions [7].

Three-Dimensional Structural Analysis: Three-dimensional molecular modeling performed using UCSF ChimeraX enabled a detailed investigation of the spatial organization of 4,4′-MDI, 1,4-butanediol, and the resulting polyurethane macromolecules. The molecular models provided valuable insights into the structural features governing the performance of the synthesized polyurethane. The simulation results demonstrated that the mechanical properties of the material are directly correlated with the number of urethane linkages, the strength of intermolecular hydrogen bonding, and the spatial distribution of the hard segments within the segmented polymer network. The enhanced ordering of hard domains and stronger intermolecular interactions contributed to the improved tensile strength, stiffness, and structural integrity of the polyurethane matrix.

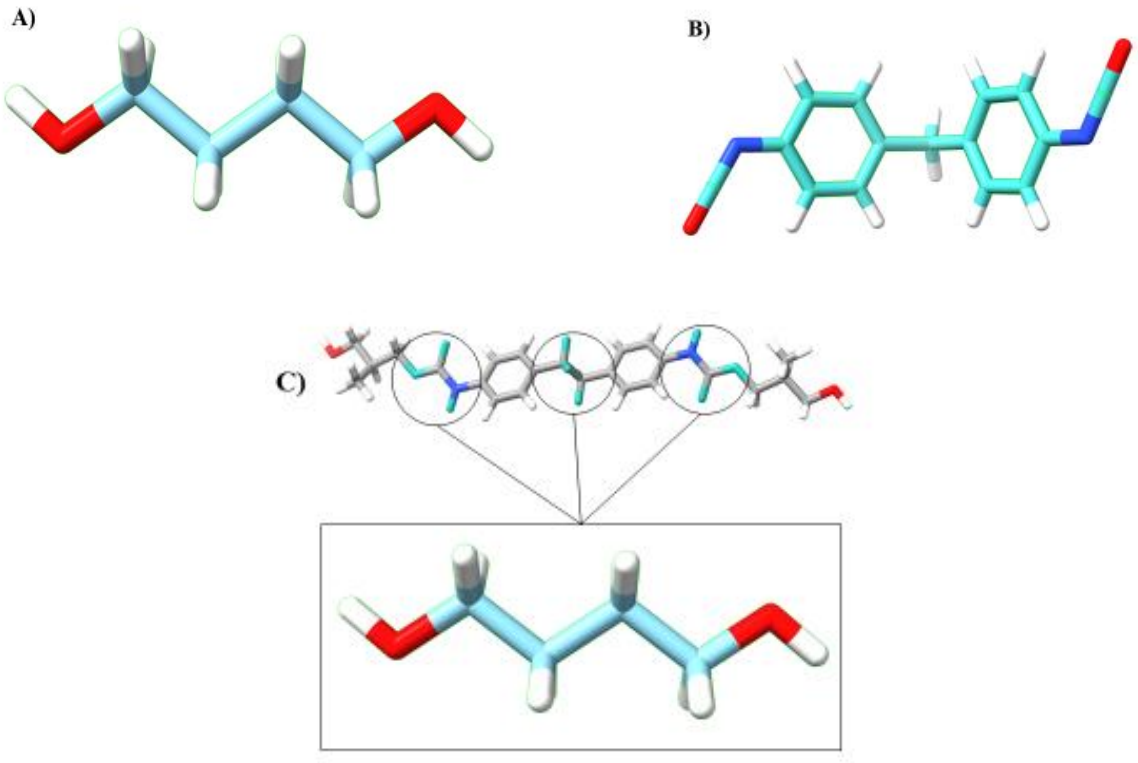

Figure 2. a) 1,4-butanediol, b) 4,4'-methylenediphenyldiisocyanate, c) polyurethane macromolecule spatial structure

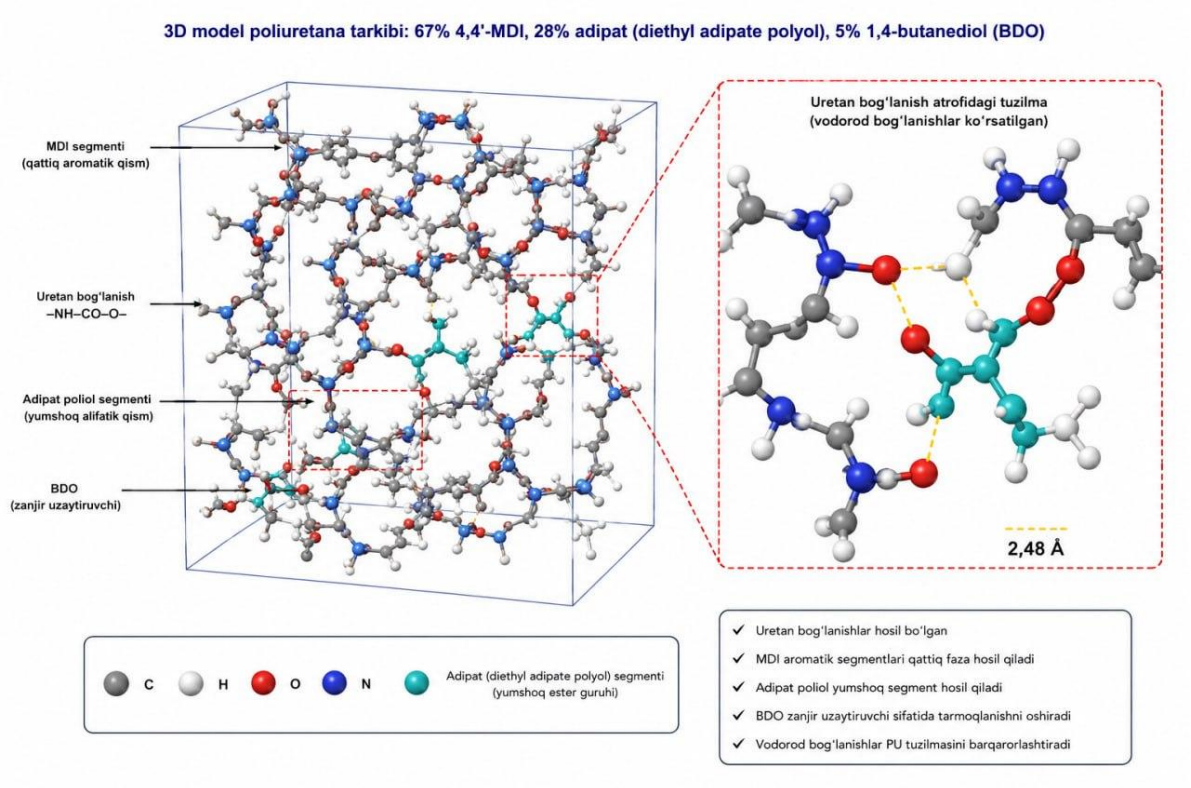

Figure 3. Three-dimensional (3D) macromolecular model of segmented polyurethane

As illustrated in Figure X, the urethane linkages (–NH–CO–O–) formed through the reaction between 4,4′-MDI and 1,4-butanediol constitute the principal structural units of the polyurethane

macromolecule. The aromatic phenylene rings of MDI form rigid hard segments with high polarity, whereas the polyester adipate chains constitute the soft segments, resulting in a characteristic microphase-separated morphology[8]. This segmented molecular architecture is one of the key structural features responsible for the outstanding elasticity, mechanical strength, and thermal stability of polyurethane materials. Intramolecular and intermolecular hydrogen bonds (approximately 2.48 Å) established between neighboring urethane groups reinforce the interactions among macromolecular chains, increase the intersegmental cohesive energy, and stabilize the three-dimensional polymer network. Consequently, the mobility of the hard-segment domains is restricted, leading to significant improvements in the elastic modulus, tensile strength, and thermo-oxidative stability of the polyurethane. Such a molecular organization represents the fundamental structural mechanism underlying the superior performance of thermosetting MDI-based polyurethanes and is widely recognized in contemporary polymer science as the characteristic structural–functional model of segmented polyurethane systems. The aromatic benzene rings present in the 4,4′-MDI molecule possess high structural rigidity and serve as the primary building blocks for the formation of hard segments within the polyurethane network. During polymerization, the isocyanate (–NCO) groups of 4,4′-MDI react with the hydroxyl (–OH) groups of 1,4-butanediol, producing urethane linkages (–NH–COO–) that form the backbone of the polyurethane macromolecule [9]. Three-dimensional molecular models generated using UCSF ChimeraX clearly demonstrate the spatial arrangement of the urethane groups and reveal the formation of hydrogen bonds between the carbonyl (C=O) and amide (N–H) groups of adjacent urethane linkages. These intermolecular interactions strengthen the attraction between hard segments, thereby increasing the elastic modulus and tensile strength of the polymer. [10][11] Molecular modeling further demonstrated that increasing the concentration of 1,4-butanediol promotes the formation of a greater number of urethane linkages, enhances hard-segment development, increases the elastic modulus, and improves Shore hardness. Nevertheless, excessive chain extender content leads to an overabundance of hard segments, restricts macromolecular mobility, and intensifies intermolecular hydrogen bonding.[12] Although these effects increase the stiffness of the polymer, they simultaneously reduce its flexibility, resulting in lower elongation at break and increased brittleness. The simulations also confirmed that the aromatic rings of 4,4′-MDI are the principal structural elements responsible for the rigidity of the polyurethane network. Their restricted rotational freedom contributes to a higher elastic modulus, while π–π interactions between neighboring aromatic rings further promote the compact packing of hard-segment domains [13. Among all structural features, the urethane linkages (–NHCOO–) were identified as the most influential factor governing the mechanical performance of the polyurethane. An increase in the concentration of urethane bonds resulted in higher tensile strength, elastic modulus, Shore hardness, and thermal stability owing to stronger intermolecular hydrogen bonding.[14] However, excessive hard-segment formation reduced macromolecular flexibility, leading to a decrease in elongation at break and a greater tendency toward brittle fracture. The three-dimensional molecular models obtained using UCSF ChimeraX enabled a comprehensive visualization of the spatial distribution of hard segments, the arrangement of urethane linkages, and the overall configuration of the polyurethane macromolecular chains. The molecular modeling results showed excellent agreement with the experimental mechanical test data and confirmed that the optimum concentration of 1,4-butanediol provides the most favorable balance between hardness, elasticity, and tensile strength in the synthesized polyurethane.[15]

Conclusion

This study investigated the influence of 1,4-butanediol as a chain extender and branched oligomers as branching agents on the macromolecular structure and physicomechanical properties of 4,4′-MDI-based polyurethanes. The experimental results demonstrated that the hydroxyl groups of 1,4-butanediol readily reacted with the isocyanate groups of 4,4′-MDI to form urethane linkages, thereby promoting polymer chain extension and increasing the proportion of hard segments within the segmented polyurethane structure. As a consequence, significant improvements were observed in tensile strength, elastic modulus, and hardness of the synthesized materials. Based on the

comprehensive analysis of the experimental data, the optimum concentration of 1,4-butanediol was determined to be 5–6 %, providing the most favorable balance between mechanical strength, elasticity, and hardness. Three-dimensional molecular modeling performed using UCSF ChimeraX enabled detailed visualization of the spatial configuration of the polyurethane macromolecules. The generated 3D molecular models facilitated the analysis of urethane bond formation, the spatial distribution of hard segments, and the role of branched oligomers in constructing the three-dimensional polymer network. The modeling results showed excellent agreement with the experimental findings and confirmed that controlled adjustment of the chain extender concentration is an effective strategy for tailoring the molecular architecture and optimizing the performance characteristics of thermosetting MDI-based polyurethane materials.

References

[1] I. N. Bakirova and T. A. Mineeva, “Sintez termoplastichnogo poliuretana s ispolzovaniem v kachestve udlinitelya tsepi aromaticheskogo diola i razrabotka na ego osnove kleevykh kompozitsiy,” *Izvestiya Vysshikh Uchebnykh Zavedeniy. Khimiya i Khimicheskaya Tekhnologiya*, vol. 67, no. 11, pp. 106–113, 2024.

[2] S. Zhao *et al*., “Poluchenie vysokomolekulyarnoy polimolochnoy kisloty na osnove tekhnologii polikondensatsii v rasplave i udlineniya tsepi,” *Journal of Applied Polymer Science*, vol. 143, no. 9, Art. no. e70150, 2026.

[3] S. Asliddin *et al*., “Izuchenie temperaturnoy zavisimosti deformatsionnykh svoystv termoreaktivnogo poliuretana s ispolzovaniem termomekhanicheskogo metoda,” *Universum: Tekhnicheskie Nauki*, no. 1–5 (106), pp. 4–7, 2023.

[4] A. F. Shodiev, “Izuchenie vliyaniya kolichestva 4,4-metildifenildiizotsianata pri pererabotke termoreaktivnykh poliuretanovykh avtokhodov,” *International Journal of Advanced Technology and Natural Sciences*, vol. 4, no. 4, pp. 47–51, 2023.

[5] L. Germán-Ayuso *et al*., “Evaluation of 2,3-butanediol derived from whey fermentation as an effective bio-based monomer for waterborne polyurethane dispersions,” *Frontiers in Chemistry*, vol. 12, Art. no. 1516427, 2025.

[6] A. Shodiev, B. Mukhiddinov, and S. Kiyomov, “Vliyanie izmeneniya kolichestva polietropoliola na fiziko-mekhanicheskie svoystva termoreaktivnogo poliuretana,” *Universum: Tekhnicheskie Nauki*, no. 10 (103), 2022.

[7] A. Slobodinyuk *et al*., “Poluchenie, struktura i svoystva uretansoderzhashchikh elastomerov na osnove epoksidnykh kontsevykh oligomerov,” *Polymers*, vol. 14, no. 3, Art. no. 524, 2022.

[8] H. L. Ornaghi *et al*., “Effect of chain extenders on the thermal and thermodegradation behavior of carbonatodiol thermoplastic polyurethane,” *Polymer Bulletin*, vol. 81, no. 3, pp. 2267–2286, 2024.

[9] P. Boisaubert *et al*., “Polyurethane coatings from formulations with low isocyanate content using a transurethane polycondensation route,” *Polymer*, vol. 240, Art. no. 124522, 2022.

[10] A. Slobodinyuk *et al*., “Preparation, structure and properties of urethane-containing elastomers based on epoxy terminal oligomers,” *Polymers*, vol. 14, no. 3, Art. no. 524, 2022.

[11] J. H. Saunders and K. C. Frisch, *Polyurethanes: Chemistry and Technology*, New York, NY, USA: Interscience Publishers, 1962.

[12] G. Oertel, Ed., *Polyurethane Handbook*, 2nd ed. Munich, Germany: Hanser Publishers, 1994.

[13] D. Randall and S. Lee, *The Polyurethanes Book*. Chichester, U.K.: John Wiley & Sons, 2002.

[14] M. Szycher, *Szycher's Handbook of Polyurethanes*, 2nd ed. Boca Raton, FL, USA: CRC Press, 2012.

[15] Z. S. Petrović, “Polyurethanes from vegetable oils,” *Polymer Reviews*, vol. 48, no. 1, pp. 109–155, 2008.