

Heat-resistant Microporous Star-shaped Casting Polyurethane for Airless Electric Bicycle Tires

Chao-Yang Yuan^{a,†}, Lei Shi^{b,†}, Shang-Chao Ji^{b,*}, Hai-Long Chen^{b,*}, Xiao Tong^b, Zi-Ying Hao^a, Xiao-Da Pan^a, Xian-Ze Yin^a, and Long Zheng^{a,*}

^a Hubei Key Laboratory for New Textile Materials and Applications, College of Materials Science and Engineering, Wuhan Textile University, Wuhan 430200, China

^b Innovation Research Institute of Zhejiang Hexin Holding Co., Ltd., Zhejiang Hexin Science and Technology Co., Ltd., Jiaxing 314001, China

Electronic Supplementary Information

Abstract Airless tires are essential for enhancing the safety, reliability, and convenience of maintenance of electric bicycles. Polyurethane (PU) is considered a promising candidate for such applications owing to its versatile properties. However, their use is limited by insufficient heat resistance and excessive dynamic heat generation under cyclic loading. In this study, star-shaped trifunctional polypropylene glycerol (PPG3) was incorporated into conventional poly(tetramethylene glycol) (PTMG) and 4,4'-methylenediphenyl diisocyanate (MDI)-based systems to construct microporous star-shaped casting polyurethanes (SCPU), with water serving as a green foaming agent. Unlike conventional small-molecule trifunctional crosslinkers that create junctions within hard segment domains, PPG3 introduces long flexible arms between the hard segments, anchoring the crosslinking points at its molecular core. The large steric hindrance of PPG3 effectively suppresses soft segment crystallization and lowers the degree of microphase separation, whereas the crosslinked network restricts chain mobility, thereby reducing dynamic heat generation. These structural features also enhance the heat resistance, yielding a softening temperature of 183 °C, which is 30.9% higher than that of polyurethane without PPG3. When applied to airless tires by casting SCPU into rubber treads, the fabricated hybrid airless tires achieved a rolling distance of over 3000 km under a load of 65 kg at 25 km/h without structural failure, satisfying practical performance requirements. This strategy offers a simple, solvent-free, and environmentally friendly process, underscoring the potential of SCPU for scalable production of high-performance airless tires.

Keywords Microporous star-shaped casting polyurethane; Microphase separation; Heat resistance; Airless tire

Citation: Yuan, C. Y.; Shi, L.; Ji, S. C.; Chen, H. L.; Tong, X.; Hao, Z. Y.; Pan, X. D.; Yin, X. Z.; Zheng, L. Heat-resistant microporous star-shaped casting polyurethane for airless electric bicycle tires. *Chinese J. Polym. Sci.* 2026, 44, 474–484.

INTRODUCTION

Electric bicycles (e-bicycles) have emerged as a sustainable and environmentally friendly option for short-distance urban transport and have become a dominant choice for daily commuting. By the end of 2024, the number of e-bicycles in China is projected to reach approximately 400 million. Within an e-bicycle system, tires are the only components in direct contact with the ground, and their safety, durability, and environmental sustainability are therefore of critical importance. The rapid expansion of e-bicycle sharing systems has accelerated the adoption of airless tires, which eliminates the risk of blowouts inherent to pneumatic tires and reduces maintenance requirements. Currently, most commercial airless tires are fabricated using foamed

rubber composites. However, vulcanization of such materials generates substantial amounts of volatile organic compounds (VOCs), raising serious environmental concerns.^[1] In contrast, polyurethane (PU) elastomers avoid such harmful emissions during processing and simultaneously offer high strength, excellent resilience, and superior wear resistance, making them highly promising candidates for airless tire fabrication.^[2] Despite these advantages, inadequate heat resistance remains a critical barrier for the broader use of PU tires.^[3] Under continuous dynamic friction with road surfaces, PU materials rapidly heat up, leading to softening, accelerated wear, and ultimately, tire failure. To mitigate this issue, hybrid airless tires have been developed by combining PU cores with rubber treads, which shield PU from direct road friction.^[4] Although this approach delays wear, it does not fundamentally improve the intrinsic heat resistance of PU, thereby limiting the long-term reliability of such systems.

PU elastomers are typically synthesized from long-chain polyols, diisocyanates, and chain extenders. Polyols generate flexible soft segments, whereas diisocyanates and chain ex-

* Corresponding authors, E-mail: shangchaoji@163.com (S.C.J.)

E-mail: krccchl@163.com (H.L.C.)

E-mail: lzheng@wtu.edu.cn (L.Z.)

[†] These authors contributed equally to this work.

Received September 8, 2025; Accepted October 27, 2025; Published online December 25, 2025

tenders form rigid hard segments. The intrinsic incompatibility between these segments drives the microphase separation.^[5–8] Among the structural variables, the chemistry of the hard segment plays a decisive role in governing the heat resistance.^[9] Aromatic diisocyanates generally afford higher thermal stability than aliphatic analogs, as their high molecular symmetry and rigidity facilitate more ordered packing of hard domains, thereby increasing the melting point and enhancing heat resistance; this is exemplified by specialty aromatic diisocyanates such as naphthalene diisocyanate (NDI), tolylene-2,4-diisocyanate (TODI), and p-phenylene diisocyanate (PPDI).^[10–13] For example, Hu *et al.* synthesized PU elastomers from polycarbonate diol (PCDL), NDI, and 1,4-butanediol (BDO), achieving a softening temperature of 204 °C combined with excellent wear and wet skid resistance and low rolling resistance.^[14] These properties highlight their potential for high-performance tire applications. Nevertheless, the practical application of these specialty aromatic diisocyanates remains restricted by their high cost, elevated melting points that complicate synthesis, and poor storage stability of the corresponding prepolymers due to their strong electrophilicity.^[15] These factors hinder the scalability of the e-bicycle tires. Thus, the development of high-heat-resistant PUs based on low-cost, commercially available diisocyanates, such as 4,4'-diphenylmethane diisocyanate (MDI), is a critical research objective.

The introduction of crosslinked networks is another effective strategy for enhancing the heat resistance of PU. Multifunctional small-molecule crosslinkers (functionality ≥ 3), such as glycerol and trimethylolpropane, can establish chemical crosslinking networks within hard segments, thereby regulating microphase separation and enhancing material properties by promoting more ordered hydrogen bonding in the hard domains.^[16–18] However, excessive hydrogen bonding and rigid crosslinked networks can restrict molecular conformational adjustments under dynamic conditions,^[19] resulting in internal heat accumulation, premature softening, thermal degradation, and brittle fracture during prolonged or high-speed cyclic running.

Star-shaped polyols are a class of highly functional polyols consisting of a central core with multiple polymeric arms, endowing them with unique spatial configuration and reactivity.^[20,21] The incorporation of star-shaped polyols yields star-shaped PUs with well-defined branched or crosslinked structures that improve the mechanical strength, thermal stability, and shape-memory behavior.^[22–24] For instance, in poly(propylene glycol) (PPG)-based PU systems, the introduction of trifunctional poly-propylene glycerol (PPG3) facilitates the preparation of star-shaped PUs with higher softening temperatures and enhanced shape memory properties.^[24] From a molecular design perspective, the introduction of star-shaped polyols relocates crosslinking points from the hard segments to the star-core, introducing long flexible arms between the hard domains. This configuration reduces the stress concentration in the hard segments and enhances the fatigue resistance. Consequently, star-shaped PUs are expected to hold significant promise for the development of high-performance airless tires for e-bicycle applications.

In this study, a star-shaped casting polyurethane (SCPU) was rationally designed and synthesized using thermally stable polytetramethylene ether glycol (PTMG) as the soft segment, MDI as the isocyanate component, PPG3 as the crosslinker, and water as a green foaming agent. The influence of the PPG3 content on the microphase structure, thermal behavior, and dynamic and static mechanical performance was systematically investigated. The results demonstrated that PPG3 incorporation effectively reduced the dynamic loss while significantly enhancing the heat resistance, with the resulting SCPU exhibiting a softening temperature of 183.0 °C. Based on these results, SCPU with the optimal PPG3 content was molded into rubber tread structures to fabricate airless tires. Rolling tests under industrial standards confirmed that tires maintained outstanding performance over distances exceeding 3000 km, underscoring their potential for practical application in e-bicycle systems.

EXPERIMENTAL

Materials

PTMG ($M_n=2000$ g/mol) and PPG3 ($M_n=700$ g/mol) were supplied by Xiaoxing Chemical Co., Ltd. (Jiaxing, China). MDI was purchased from Wanhua Chemical Group Co., Ltd. (Shandong, China). *N,N*-Dimethylformamide (DMF) and triethylenediamine (TEDA) were obtained from Aladdin Reagent Co., Ltd. (Shanghai, China). Deionized water was prepared in the laboratory.

Preparation of SCPU

The synthesis route for SCPU is illustrated in Fig. 1. Initially, a predetermined amount of PTMG was placed in a three-neck flask and subjected to vacuum drying at -0.1 MPa and 120 °C for 2 h. After dehydration, the system was cooled to 60 °C, followed by addition of a stoichiometric amount of MDI. The mixture was stirred under nitrogen atmosphere for 2 h to obtain the isocyanate-terminated PTMG-MDI prepolymer, denoted as component A. The mass ratio of MDI to PTMG was 6:4.

Subsequently, PTMG and PPG3 were mixed in mass ratios of 100:0, 95:5, 90:10, 85:15, and 80:20. Deionized water (0.22 g) and the TEDA catalyst (1 g) were sequentially added, and the mixture was stirred thoroughly to produce component B. Components A and B were then mixed according to the designed ratios and rapidly stirred for 30 s, during which the mixture volume expanded markedly, followed by immediate casting into preheated polytetrafluoroethylene molds. The samples were cured in an oven at 80 °C for 2 h to obtain the microporous SCPU. The overall hydroxyl-to-isocyanate molar ratio was maintained at 1.04:1 to ensure the complete reaction of the isocyanate groups. The detailed formulations are presented in Table 1. The sample without PPG3 was designated as CPU. The as-prepared SCPU samples were labeled SCPUx according to the mass fraction of PPG3 incorporated; for example, SCPU3.8 indicates 3.8 wt% PPG3 in the system.

Preparation of SCPU-based Hybrid Airless Tires

To evaluate the practical applicability of SCPU in industry, airless tires were fabricated at Zhejiang Hexin Science and Technology Co., Ltd. (Jiaxing, China) using the SCPU10.7 formulation. A 15.75-inch rubber tire tread was employed as the mold, and an automatic casting machine was used to produce microporous SCPU-filled hybrid airless tires.

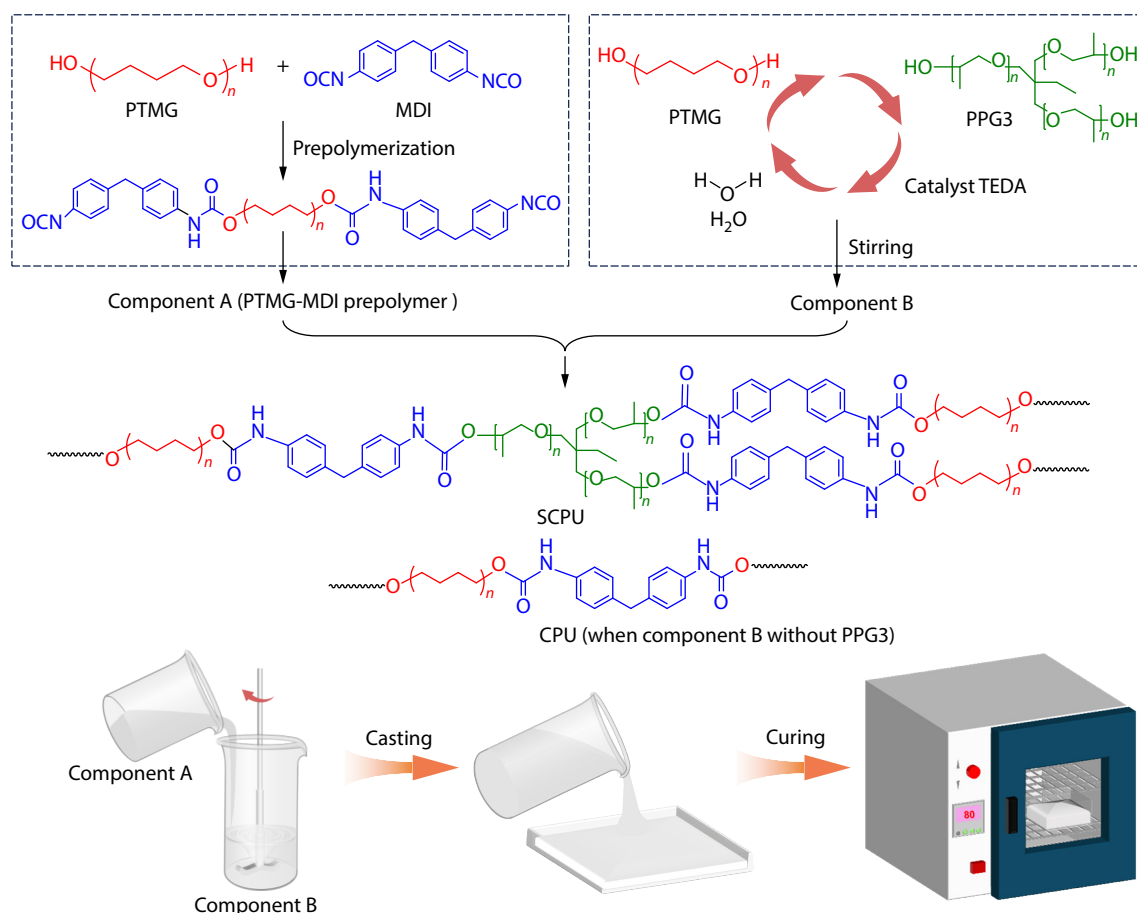


Fig. 1 Synthesis routes of SCPU.

Table 1 Synthesized formulation of CPU and SCPU samples (mass and mass ratio).

Sample		CPU	SCPU3.8	SCPU7.4	SCPU10.7	SCPU13.9
Component A (g)	PTMG	40	40	40	40	40
	MDI	60	60	60	60	60
Component B (g)	PTMG	100	95	90	85	80
	PPG3	0	5	10	15	20
	H ₂ O	0.22	0.22	0.22	0.22	0.22
	TEDA	1	1	1	1	1
Mass ratio of A/B		29.2/100	33.0/100	36.9/100	40.7/100	44.6/100

Characterization

The microporous morphologies of the samples were examined by scanning electron microscopy (SEM, Hitachi SU5000, Japan). The chemical structures were characterized by Fourier transform infrared spectroscopy in the attenuated total reflectance mode (ATR-FTIR, TENSORII, Bruker, Germany) over 4000–450 cm⁻¹. Microphase separation was investigated by atomic force microscopy (AFM, MultiMode 8-HR, Bruker, Germany) operated in the Quantitative Nanomechanical Mapping (QNM) mode; samples were cryo-fractured in liquid nitrogen and polished to obtain flat surfaces prior to imaging. The crystallinity was analyzed by X-ray diffraction (XRD, D/max 2500, Japan) over a 2θ range of 5°–50°. Thermal behavior was analyzed by differential scanning calorimetry (DSC, DSC1, Mettler-Toledo, Switzerland) under nitrogen using the following program: heating from 25 °C to 250 °C, cooling to –70 °C, and reheating to 250 °C at a rate of 10 °C/min, with a 5 min isothermal hold at each temperature

step. The softening temperature was determined by thermo-mechanical analysis (TMA, TMA-60, Shimadzu, Japan) using a cylindrical probe under a constant load of 1 N and heated from 30 °C to 200 °C at 5 °C/min. Thermal stability was assessed by thermogravimetric analysis (TGA, STARe TGA, Mettler-Toledo, Switzerland) under nitrogen from 30 °C to 800 °C at a heating rate of 10 °C/min. The dynamic mechanical properties were measured in compression mode using a dynamic mechanical analyzer in compression mode (DMA, Q800, TA Instruments, USA) with a temperature sweep from 25 °C to 150 °C at 1 Hz. The Compression stress-strain behavior was obtained using an Instron 4465 universal testing machine (Instron Corp., USA) at room temperature. The rolling durability of the SCPU airless tires was assessed using a custom-built testing apparatus designed to simulate the e-bicycle operating conditions. During the test, each tire was subjected to a load of 65 kg and rolled at a constant speed of 25 km/h; the continuous rolling distance was

recorded.

RESULTS AND DISCUSSION

The Construction and Chemical Structure Characterization of Micro Porous SCPUs

To develop lightweight and comfortable tires, the incorporation of microcellular structures into polyurethane matrices is an effective strategy to reduce density while enhancing elasticity. In the present system, water acted as a reactive foaming agent. Upon mixing components A and B, water molecules in component B reacted rapidly with isocyanate groups (—NCO) to generate an unstable carbamate intermediate (R—NH—COOH), which decomposed into primary amines with the concurrent release of CO_2 . The evolution of CO_2 created gas bubbles, driving the formation of a microcellular morphology. The newly formed amines subsequently reacted with the residual —NCO groups to form urea linkages, further contributing to network crosslinking. As the curing progressed, the microcellular structure gradually stabilized, yielding a permanent microporous architecture.

The microcellular structures of the CPU and SCPUs were examined using SEM, as shown in Fig. 2. In the CPU sample without PPG3, the pores appeared irregular, most likely due to the collapse or deformation of the cellular structure during curing as a result of polymer flow. With the incorporation of PPG3, the pore morphology in SCPUs became progressively more uniform, indicating that PPG3 stabilized the microcellular framework. Quantitative pore size analysis showed that the average pore diameter increased slightly from 153 μm to 173 μm as the PPG3 content increased from 3.8 wt% to 13.9 wt%. Despite this modest enlargement, the distribution became significantly homogeneous. Such uniformity effectively reduces the localized stress concentrations associated with irregular pore sizes and contributes to the improved mechanical stability of the material. The porosities of CPU, SCPU3.8, SCPU7.4, SCPU10.7, and SCPU13.9 were determined to be 50.9%, 55.5%, 56.4%, 59.1%, and 59.1%, respectively, indicat-

ing that all foamed samples with PPG3 maintained a relatively stable porosity.

The introduction of PPG3 introduces star-shaped junctions that promote the formation of a chemically crosslinked network within the polyurethane matrix. Unlike small-molecule trifunctional polyols, whose crosslinking points are typically localized in the hard segment domains, the crosslinking sites of PPG3 reside at the molecular core, thereby distributing the network more uniformly. Such a network prevents the polymer from fully dissolving in good solvents and restricts its swelling behavior. To verify this effect, dissolution and swelling experiments were performed in DMF, a strong solvent for linear polyurethanes. As shown in Fig. 3, the CPU sample without PPG3 completely dissolved after 24 h, yielding a transparent solution, which is consistent with its linear molecular architecture. In contrast, the SCPUs containing PPG3 remained intact even after 72 h, exhibiting varying degrees of swelling rather than dissolution, thereby confirming the establishment of crosslinked networks. Notably, SCPU3.8 displayed a relatively loose structure upon swelling, reflecting its lower crosslink density. With increasing PPG3 content to 10.7 wt% and 13.9 wt%, the volumetric changes became significantly reduced, indicating the development of a denser three-dimensional network that effectively limited solvent penetration and polymer chain expansion.

The chemical structures of CPU and SCPUs were investigated using ATR-FTIR spectroscopy (Fig. 4a). The absorption bands at 2937 and 2849 cm^{-1} correspond to the asymmetric and symmetric stretching vibrations of the —CH_2 groups, respectively.^[25] The characteristic band at 1598 cm^{-1} was assigned to the $\text{C}=\text{C}$ stretching vibration of the aromatic ring in MDI.^[26] The band at 1100 cm^{-1} arises from the C—O—C stretching vibration of PTMG and PPG3.^[27] The band observed at 3296 cm^{-1} originates from the N—H stretching vibration of urethane groups, whereas the band at 1530 cm^{-1} corresponds to the amide II vibration, associated with both C—N stretching and N—H bending vibrations.^[28] The car-

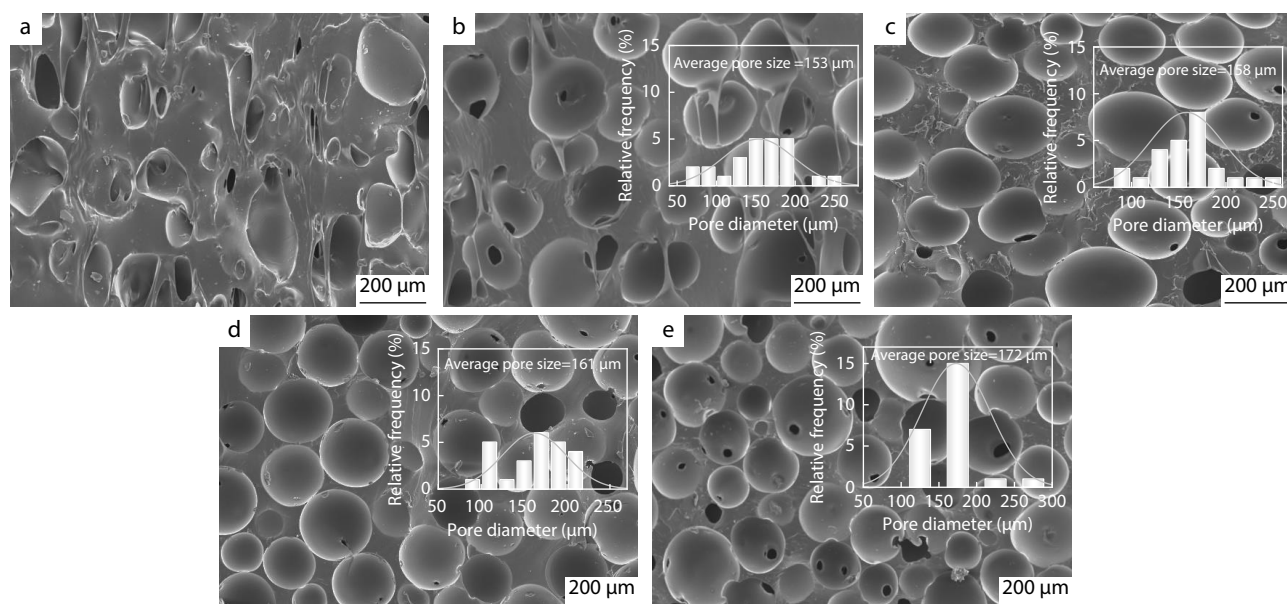


Fig. 2 SEM images of (a) CPU, (b) SCPU3.8, (c) SCPU7.4, (d) SCPU10.7, and (e) SCPU13.9. Insets display the corresponding pore size distributions.

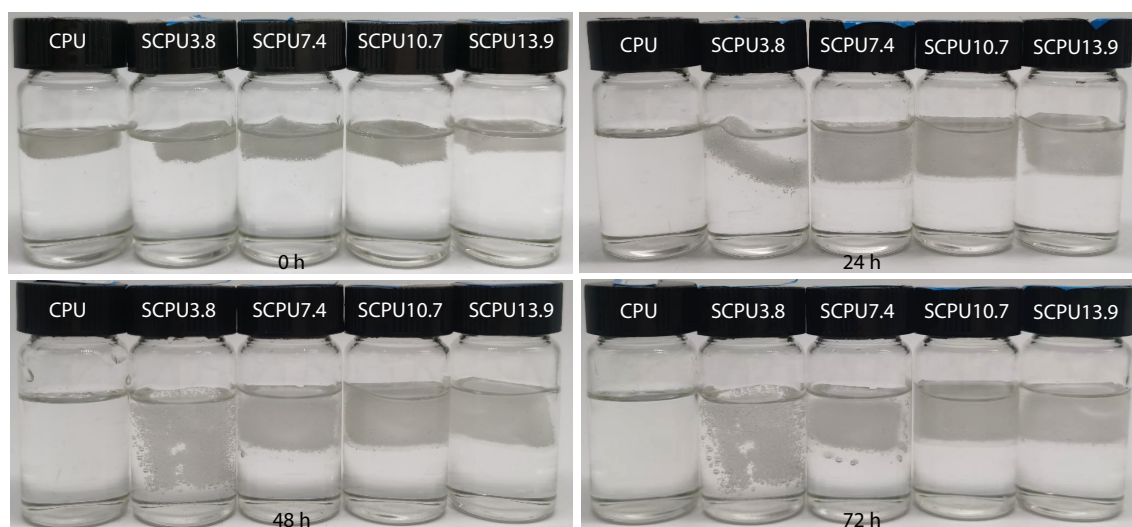


Fig. 3 Photographs showing dissolution and swelling behavior of CPU and SCPUs immersion in DMF for different durations.

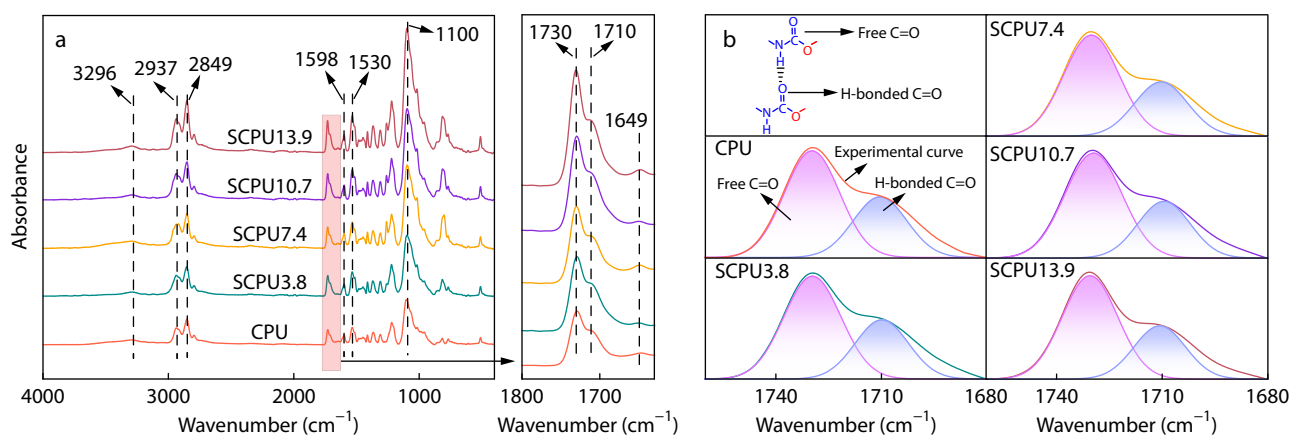


Fig. 4 (a) FTIR spectra of CPU and SCPUs; (b) Curve-fitted carbonyl region used for hydrogen-bonding analysis.

bonyl stretching vibration ($\text{C}=\text{O}$) was observed between 1780 and 1640 cm^{-1} . This band split into two distinct components owing to hydrogen bonding. The band at 1730 cm^{-1} is attributed to free $\text{C}=\text{O}$ groups not engaged in hydrogen bonding, whereas the shoulder band at 1710 cm^{-1} corresponds to hydrogen-bonded $\text{C}=\text{O}$ groups.^[29] A weak band at 1649 cm^{-1} was also detected, which was assigned to the $\text{C}=\text{O}$ stretching of urea linkages formed *via* the reaction between water and isocyanate.^[30] The absence of the $-\text{NCO}$ absorption band at 2270 cm^{-1} in all the spectra confirms the complete consumption of the isocyanate groups.^[31]

To further elucidate the hydrogen-bonding interactions, the carbonyl region was deconvoluted and the ratio of hydrogen-bonded to free $\text{C}=\text{O}$ peak areas was calculated (Fig. 4b).^[32,33] With increasing PPG3 content, these ratios decreased from 0.552 to 0.479, indicating progressive reduction in hydrogen bonding. This trend is attributed to the steric hindrance introduced by the long flexible arms of PPG3 and the methyl groups along each arm, both of which impede hydrogen bond formation.

Microphase Separation and Crystalline Structure of SCPUs

The microphase separation structure of the CPU and SCPUs was

further investigated using AFM in QNM mode. In the DMT modulus images (Fig. 5), the color scale from bright to dark reflects the modulus values from high to low. The bright island-like regions correspond to the hard segment domains with a higher modulus, whereas the darker regions represent the soft segment matrix.^[34] For the CPU sample, densely aggregated hard segments with relatively narrow spacing were observed, indicating pronounced microphase separation. Upon incorporation of PPG3, hard segment aggregation remained visible in SCPU3.8 and SCPU7.4, although the overall DMT modulus values decreased. When the PPG3 content was further increased to 10.7% and 13.9%, the abundance of hard segment-rich domains was markedly reduced and only sparse bright spots were dispersed within the soft segment matrix. This reduction in phase-separated domains can be attributed to the steric hindrance introduced by the long flexible arms of PPG3, which suppressed the hard segment aggregation. Additionally, the formation of a crosslinked network restricts the mobility of PU chains, thereby further inhibiting microphase separation between the hard and soft segments.^[35]

DSC was employed to further elucidate the microphase separation and crystallization behavior of CPU and SCPUs. As shown in Fig. 6, the glass transition temperature (T_g), melting

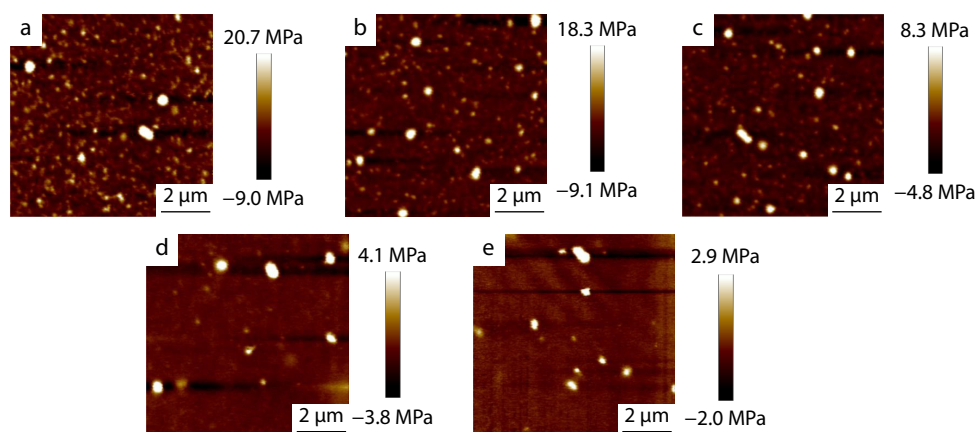


Fig. 5 PeakForce QNM AFM images of (a) CPU, (b) SCPU3.8, (c) SCPU7.4, (d) SCPU10.8, and (e) SCPU13.9.

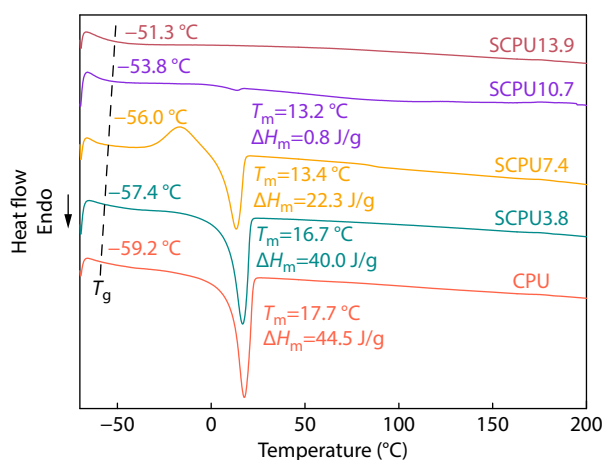


Fig. 6 DSC thermograms of CPU and SCPUs.

temperature (T_m), and melting enthalpy (ΔH_m) of each sample were obtained from the DSC curves. The T_g values progressively increased with the incorporation of PPG3, rising from -59.2 °C for CPU to -51.3 °C for SCPU13.9. This increase is attributed to the formation of a crosslinked structure, which restricts the mobility of the polyurethane chains and consequently elevates T_g . For a linear CPU, the ordered molecular structure of PTMG allows the formation of crystalline regions within the soft segments, as evidenced by the DSC result of pure PTMG showing a melting peak at 22.7 °C with a ΔH_m of 86.1 J/g (Fig. S1 in the electronic supplementary information, ESI). Accordingly, CPU exhibited a melting peak at $T_m = 17.7$ °C with $\Delta H_m = 44.5$ J/g. Upon introducing PPG3, both T_m and ΔH_m decreased gradually, reflecting the reduced crystallization capability of the soft segments. For instance, SCPU10.7 displayed a T_m of 13.2 °C with a ΔH_m as low as 0.8 J/g, indicating that crystallization was almost completely suppressed. At a PPG3 content of 13.9%, no detectable melting peak was observed, confirming the disappearance of soft segment crystallinity. This phenomenon can be ascribed to the steric hindrance imposed by the long flexible PPG3 arms and crosslinked network, which impedes the ordered packing of soft segments into crystalline domains.

XRD analysis was conducted to further verify the crystallization behavior identified by DSC. As shown in Fig. 7, all the

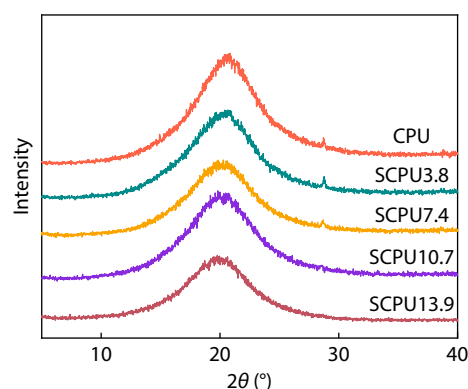


Fig. 7 XRD patterns of CPU and SCPUs.

samples exhibit a broad amorphous diffraction peak around approximately 2θ equal to 20° , indicating that the polymer chains predominantly exist in an amorphous and disordered state. With increasing PPG3 content, the intensity of this peak gradually decreased and broadened, suggesting progressive enhancement of the structural disorder within the PU matrix. In addition to the amorphous peak, CPU displayed a weak crystalline diffraction peak at $2\theta = 28.7^\circ$, which was attributed to the crystallization of PTMG soft segments, as confirmed by the XRD pattern of pure PTMG (Fig. S2 in ESI). However, this crystalline feature completely disappears in SCPU13.9, which is consistent with the DSC results and confirms that the incorporation of PPG3 effectively suppresses soft-segment crystallinity.

Thermal Properties of SCPUs

TMA was employed to evaluate the heat resistance of the samples by monitoring dimensional changes under non-oscillatory stress as a function of temperature. The TMA curves of the CPU and SCPUs are shown in Fig. 8(a) and the corresponding softening temperatures are summarized in Fig. 8(b). A clear trend was observed in that the softening temperature of the SCPUs increased markedly with increasing PPG3 content. Specifically, SCPU10.7 and SCPU13.9 exhibit softening temperatures of 183.0 and 186.3 °C, corresponding to enhancements of 30.9% and 33.3% relative to the CPU, respectively. Although the introduction of PPG3 increases the spacing between the hard segments and reduces their interactions, the formation of a crosslinked

network stabilizes the polymer matrix and preserves the structural integrity at elevated temperatures. Such an enhancement is particularly critical under the high-speed dynamic conditions encountered in e-bicycle tire applications.

TGA was performed to investigate the thermal degradation behavior of the CPU and SCPUs. The TGA and derivative thermogravimetry (DTG) curves are shown in Figs. 9(a) and 9(b), and the corresponding parameters, including the onset decomposition temperature ($T_{5\%}$), multistage weight losses, and char residues at 800 °C, are summarized in Table 2. For the CPU, the $T_{5\%}$ value is 323.0 °C, with two distinct weight-loss stages evident in the DTG curve. The first stage, centered at approximately 355 °C, is attributed to the decomposition of hard segments, whereas the second stage, occurring near 419 °C, corresponds to the degradation of soft segments.^[36] After the incorporation of PPG3, the $T_{5\%}$ values of the SCPUs decreased slightly to approximately 313 °C, suggesting a mod-

est reduction in the initial decomposition resistance. The degradation process of SCPUs retains a two-stage profile, and the weight loss in both stages gradually increases with increasing PPG3 content. The char residues of all the samples remained below 2% at 800 °C, confirming that the thermal degradation of these systems primarily proceeds through volatilization rather than carbonaceous residue formation. Despite the slight decrease in $T_{5\%}$, the SCPUs maintained high overall thermal stability, which is sufficient for their targeted application in e-bicycle tires.

Dynamic Compression Loss Behavior of SCPUs

The temperature rise of tires during driving is primarily induced by the lag of polymer chain segments, which leads to energy dissipation and dynamic heat buildup. DMA provides a sensitive approach to probe such thermo-mechanical behavior by applying small-amplitude periodic loads under controlled temperatures, while simultaneously recording the stress-strain re-

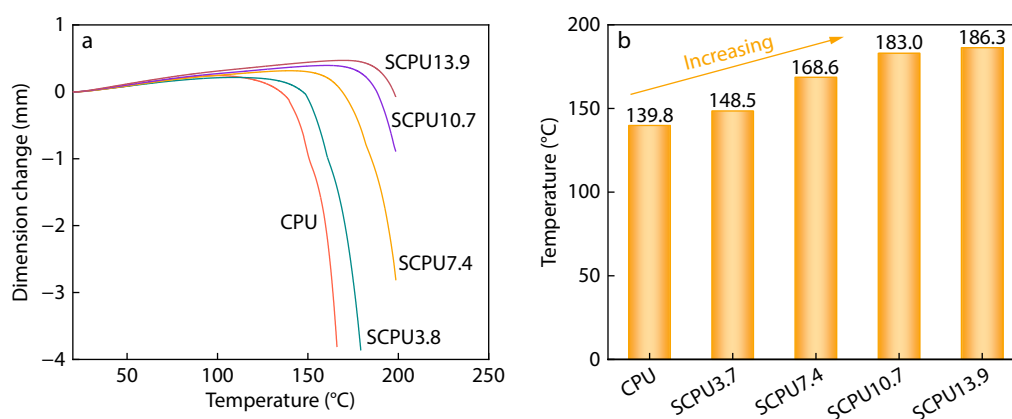


Fig. 8 (a) TMA curves and (b) softening temperatures of CPU and SCPUs.

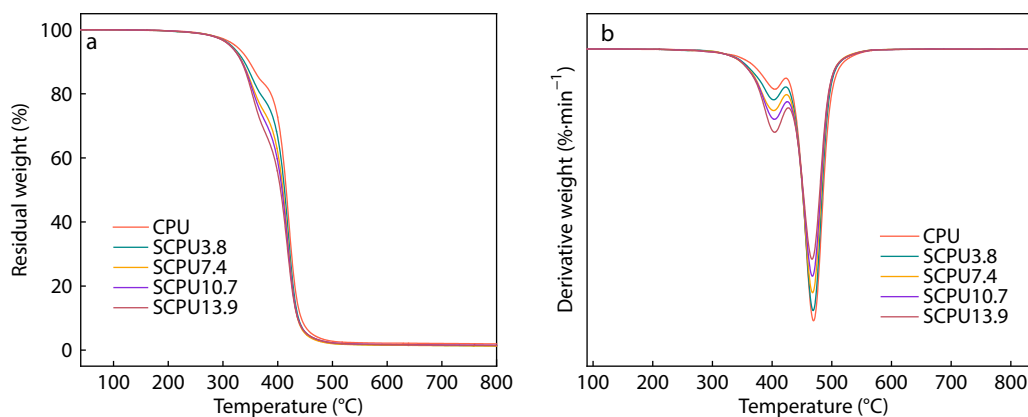


Fig. 9 (a) TGA and (b) DTG curves of CPU and SCPUs.

Table 2 Multi-stage thermal weight loss data of CPU and SCPUs.

Sample	Weight loss (%)		Char residue (%)	$T_{5\%}$ (°C)
	Stage 1	Stage 2		
CPU	12.0	58.1	1.9	323.0
SCPU3.8	15.6	63.8	1.3	315.5
SCPU7.4	18.1	67.6	1.3	313.7
SCPU10.7	19.2	68.9	1.5	313.3
SCPU13.9	20.9	71.0	1.5	313.0

sponse. This enabled the quantitative evaluation of the viscoelastic parameters. DMA was performed in the compression mode because the SCPU material functions as a core filler inside the rubber tread of the airless tire, where it predominantly undergoes periodic vertical compressive loads during rolling. The loss factor ($\tan\delta$)-temperature curves for the CPU and SCPUs are shown in Fig. 10. For CPU, $\tan\delta$ remained relatively stable below 70 °C, suggesting low internal dissipation and a stable viscoelastic response. However, above 70 °C, $\tan\delta$ increases sharply, reflecting the enhanced chain mobility of the segments that increases internal friction, thereby accelerating energy dissipation and heat accumulation. SCPU3.8 and SCPU7.4 also exhibit an upward trend in $\tan\delta$ at elevated temperatures, yet their overall values remain markedly lower than those of the CPU, indicating a partial suppression of dynamic loss. Strikingly, SCPU10.7 and SCPU13.9 maintained low and stable $\tan\delta$ values over the entire temperature range, demonstrating superior resistance to elevated temperatures under dynamic conditions. This improved performance is attributed to the presence of the crosslinked

network introduced by PPG3, which effectively restricts the mobility of chains and limits lag-induced heat generation. This suppression of dynamic compression loss is highly beneficial for extending the service life of e-bicycle tires under high-speed and long-distance cycling conditions.

Compressive Mechanical Properties

Fig. 11 shows the compressive stress-strain curves of the CPU and SCPUs. All the samples exhibited a typical nonlinear response that could be divided into three characteristic stages. In the initial strain range, the stress increases almost linearly with strain, reflecting the cooperative stretching of polymer chains and the corresponding elastic recovery of the material. As deformation progressed, the soft segment chains underwent significant sliding and rearrangement, and partial disruption of the microphase structures occurred. This marks the transition from predominantly elastic behavior to plastic flow. At high strains, the internal pores and free volume were nearly exhausted, and the spacing between the molecular chains was significantly re-

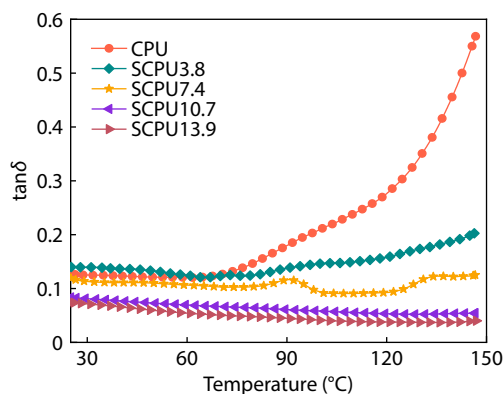


Fig. 10 $\tan\delta$ versus temperature curves of CPU and SCPUs.

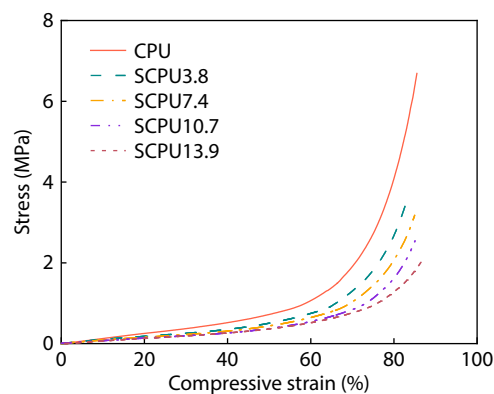


Fig. 11 Compressive stress-strain curves of CPU and SCPUs.

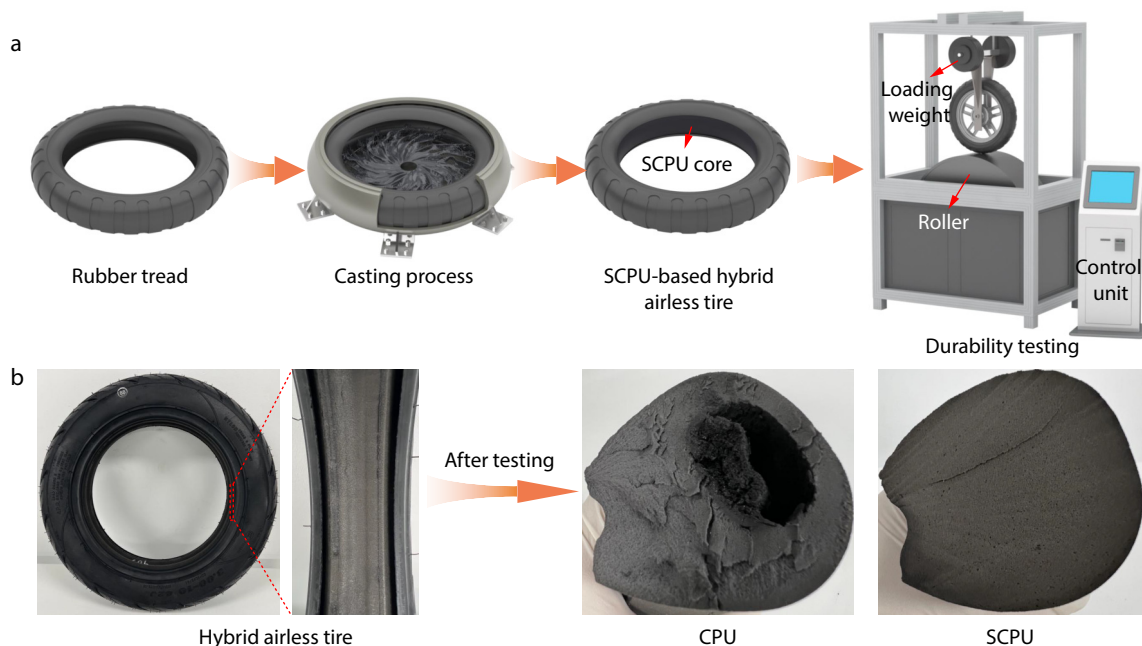


Fig. 12 (a) Preparation process of SCPU-based hybrid airless tires and schematic of the durability testing setup; (b) Photographs of the hybrid airless tire, along with cross-sectional images of the CPU and SCPU cores after durability test.

duced. Consequently, the stress increases sharply with further strain. At approximately 85% compression, the material reached a dense state. The corresponding stress values at this dense state are 6.7 MPa for CPU, and 3.5, 3.2, 2.5, and 2.0 MPa for SCPU3.8, SCPU7.4, SCPU10.7, and SCPU13.9, respectively. The progressive reduction in compressive stress with increasing PPG3 content was attributed to the influence of the star-shaped crosslinked network, which reduced the crystallinity of the soft segments. Despite the reduction in compressive strength with increasing PPG3 content, SCPU materials still provide adequate mechanical support for their intended application in airless tires, ensuring structural integrity under typical load conditions.

Evaluation of the Durability of SCPU-based Hybrid Airless Tires

Given the superior heat resistance and low dynamic heat generation of SCPU, it exhibits strong potential for application in airless tires. To evaluate its practical performance, the SCPU10.7 formulation was selected based on its overall optimized performance. To prevent the inherent yellowing of aromatic polyurethane during service, a black pigment was incorporated into the formulation to produce a uniformly black core. The resulting material was cast into a 15.75-inch rubber tread using an automatic casting machine to fabricate microporous airless tires. The durability of the fabricated hybrid airless tires was assessed under a load of 65 kg at a rolling speed of 25 km·h⁻¹, as shown in Fig. 12(a). Both CPU- and SCPU-based tires were continuously rolled under these conditions to compare their performances. The CPU-based hybrid tire failed after only 10 km, and the cross-sectional inspection revealed severe melting and structural damage to the CPU core (Fig. 12b). In contrast, the SCPU-based hybrid airless tire rolled continuously for over 3000 km, and cross-sectional inspection after testing revealed no structural damage (Fig. 12b). These findings demonstrate the excellent mechanical stability and practical applicability of the SCPU-based design for high-performance and durable e-bicycle applications.

CONCLUSIONS

In summary, a series of microporous SCPU was successfully prepared via a casting process, employing star-shaped PPG3 as a multifunctional crosslinker and water as an environmentally friendly foaming agent. The incorporation of PPG3 generated long flexible arms between the hard-segment domains, forming a crosslinked network. The large steric hindrance of PPG3 hindered the ordering of soft and hard segments, thereby suppressing PTMG soft-segment crystallization and reducing the degree of microphase separation. The incorporation of 10.7% PPG3 increased the softening temperature of SCPU to 183 °C, exhibiting a 30.9% improvement compared to CPU. Meanwhile, the crosslinked network restricted the mobility of the polymer chains, leading to a remarkable reduction in dynamic loss. When applied to airless tires by casting SCPU into rubber treads, the rolling distance exceeds 3000 km, satisfying practical performance requirements. This approach offers a simple, cost-effective, and solvent-free route with negligible harmful emissions, highlighting the potential of SCPU for industrial-scale high-performance airless tire applications.

Conflict of Interests

The authors declare no interest conflict.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <http://doi.org/10.1007/s10118-025-3491-7>.

Data Availability Statement

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

ACKNOWLEDGMENTS

This work was financially supported by the National Natural Science Foundation of China (No. 52303063) and Hubei Provincial Department of Education Guided Scientific Research Project (No. B2024056).

REFERENCES

- Huang, H.; Wang, Z.; Dai, C.; Guo, J.; Zhang, X. Volatile organic compounds emission in the rubber products manufacturing processes. *Environ. Res.* **2022**, *212*, 113485.
- Miller, L. J.; Sawyer-Beaulieu, S.; Tam, E. Impacts of non-traditional uses of polyurethane foam in automotive applications at end of life. *SAE Int. J. Mater. Manuf.* **2014**, *7*, 711–718.
- Sun, M.; Zhong, H.; Qin, K.; Xu, T.; Yang, W.; Zhang, Y.; Lu, L. The development of processing methods and materials used for non-pneumatic tires: a review. *Materials* **2024**, *17*, 5660.
- Nandhu, S.; Jayan, A. K.; Ahmed, J. S.; Manikandan, V.; Kumar, V. S. Analysis of polyurethane filled solid tire. *Adv. Mater. Res.* **2014**, *984*, 464–468.
- Zheng, N.; Hou, J.; Xu, Y.; Fang, Z.; Zou, W.; Zhao, Q.; Xie, T. Catalyst-free thermoset polyurethane with permanent shape reconfigurability and highly tunable triple-shape memory performance. *ACS Macro Lett.* **2017**, *6*, 326–330.
- Xiang, X.; Zhang, L.; Sheng, D.; Yang, X.; Qi, X.; Wei, S.; Dai, H. Healable and recyclable polyurea-urethane elastomer with high mechanical robustness, superhigh elastic restorability, and exceptional crack tolerance. *Adv. Funct. Mater.* **2024**, *34*, 2312571.
- Cheng, B. X.; Gao, W. C.; Ren, X. M.; Ouyang, X. Y.; Zhao, Y.; Zhao, H.; Wu, W.; Huang, C. X.; Liu, Y.; Liu, X. Y.; Li, H. N.; Li, R. K. Y. A review of microphase separation of polyurethane: characterization and applications. *Polym. Test.* **2022**, *107*, 107489.
- Delavarde, A.; Savin, G.; Derkenne, P.; Boursier, M.; Morales-Cerrada, R.; Nottelet, B.; Pinaud, J.; Caillol, S. Sustainable polyurethanes: toward new cutting-edge opportunities. *Prog. Polym. Sci.* **2024**, *151*, 101805.
- Kojio, K.; Nozaki, S.; Takahara, A.; Yamasaki, S. Influence of chemical structure of hard segments on physical properties of polyurethane elastomers: a review. *J. Polym. Res.* **2020**, *27*, 140.
- Bhosale, S. V.; Al Kobaisi, M.; Jadhav, R. W.; Morajkar, P. P.; Jones, L. A.; George, S. Naphthalene diimides: perspectives and promise. *Chem. Soc. Rev.* **2021**, *50*, 9845–9998.
- Hu, S.; Shou, T.; Guo, M.; Wang, R.; Wang, J.; Tian, H.; Qin, X.; Zhao, X.; Zhang, L. Fabrication of new thermoplastic polyurethane elastomers with high heat resistance for 3D printing derived

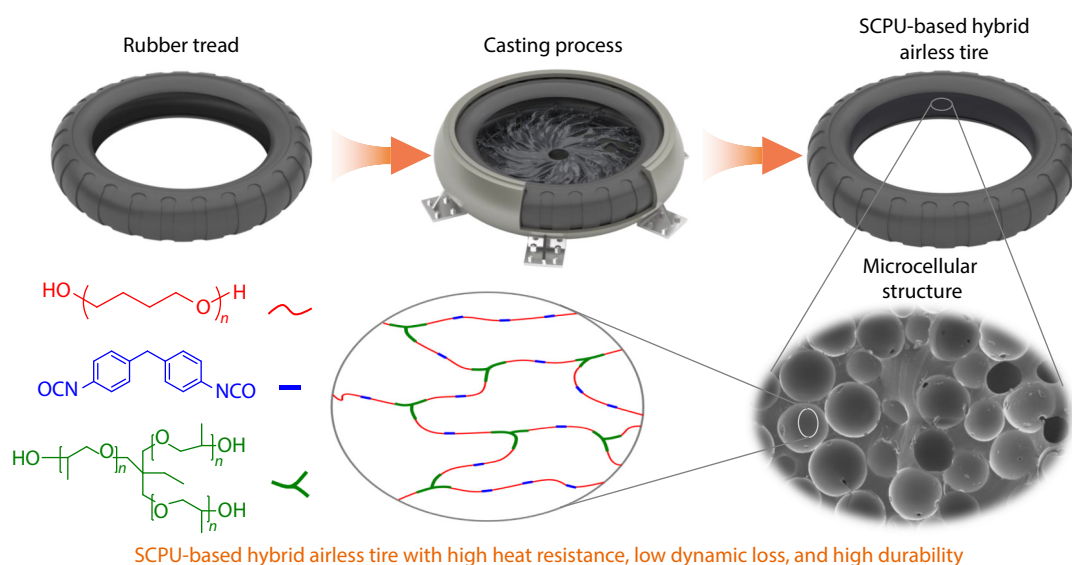
Graphical Abstract

Heat-resistant Microporous Star-shaped Casting Polyurethane for Airless Electric Bicycle Tires

Chao-Yang Yuan, Lei Shi, Shang-Chao Ji, Hai-Long Chen, Xiao Tong, Zi-Ying Hao, Xiao-Da Pan, Xian-Ze Yin, and Long Zheng

Wuhan Textile University; Zhejiang Hexin Science and Technology Co., Ltd.

In this work, star-shaped polyether polyols were employed to construct a microporous crosslinked network and to regulate the microphase separation of polyurethane. The obtained casting polyurethane shows enhanced heat resistance and reduced dynamic loss and has been successfully applied in airless electric bicycle tires.



Chinese J. Polym. Sci. 2026, 44, 474–484

<https://doi.org/10.1007/s10118-025-3491-7>

- from 3,3-dimethyl-4,4'-diphenyl diisocyanate. *Ind. Eng. Chem. Res.* **2020**, 59, 10476–10482.
- 12 Hu, S.; Shou, T.; Zhao, X.; Wang, Z.; Zhang, S.; Qin, X.; Guo, M.; Zhang, L. Rational design of a novel NDI-based thermoplastic polyurethane elastomer with superior heat resistance. *Polymer* **2020**, 205, 122764.
 - 13 Yilgor, I.; Yilgor, E.; Guler, I. G.; Ward, T. C.; Wilkes, G. L. FTIR investigation of the influence of diisocyanate symmetry on the morphology development in model segmented polyurethanes. *Polymer* **2006**, 47, 4105–4114.
 - 14 Hu, S.; He, S.; Wang, Y.; Wu, Y.; Shou, T.; Yin, D.; Mu, G.; Zhao, X.; Gao, Y.; Liu, J.; Li, F.; Guo, M.; Zhang, L. Self-repairable, recyclable and heat-resistant polyurethane for high-performance automobile tires. *Nano Energy* **2022**, 95, 107012.
 - 15 Liu, H.; Zhang, Z.; Zhu, Y.; Sun, J.; Wang, L.; Huang, T.; Chen, L. Modification of asphalt using polyurethanes synthesized with different isocyanates. *Const. Build. Mater.* **2022**, 327, 126959.
 - 16 Zhu, Y.; Zhou, C.; Liu, L.; Wu, G. Heat-resistant and high adhesion PPCD-type double crosslinked network structure waterborne polyurethane coatings. *Prog. Org. Coat.* **2024**, 197, 108858.
 - 17 Kharbas, H. A.; Ellingham, T.; Manitiu, M.; Scholz, G.; Turng, L.-S. Effect of a cross-linking agent on the foamability of microcellular injection molded thermoplastic polyurethane. *J. Cell. Plast.* **2017**, 53, 407–423.
 - 18 Song, X.; Zhou, C.; Liu, L.; Wu, G. A sulfonated hyperbranched bio-based waterborne polyurethane sizing coating for the enhancement of mechanical properties and surface wettability of carbon fibres. *Prog. Org. Coat.* **2024**, 196, 108691.
 - 19 Liu, X.; Ding, S.; Wang, F.; Shi, Y.; Wang, X.; Wang, Z. Controlling energy dissipation during deformation by selection of the hard-segment component for thermoplastic polyurethanes. *Ind. Eng. Chem. Res.* **2022**, 61, 8821–8831.
 - 20 Zhao, J.; Xu, R.; Luo, G.; Wu, J.; Xia, H. Self-healing poly (siloxane-urethane) elastomers with remoldability, shape memory and biocompatibility. *Polym. Chem.* **2016**, 7, 7278–7286.
 - 21 Wang, L.; Ding, W.; Song, K.; Dong, C.; Chen, M.; Zhou, H. Synthesis of a branched star copolymer by aqueous SET-LRP and its thermo-stimuli response. *J. Macromol. Sci. A* **2020**, 57, 266–273.
 - 22 Yang, X.; Wang, L.; Wang, W.; Chen, H.; Yang, G.; Zhou, S. Triple shape memory effect of star-shaped polyurethane. *ACS Appl. Mater. Interfaces* **2014**, 6, 6545–6554.
 - 23 Sakhavi, M.; Sofla, R. L. M.; Rezaei, M.; Miralvar, M. R. Synthesis of chemically-crosslinked multi-arm star-shaped polyurethane with triple-shape memory effect. *J. Mech. Behav. Biomed. Mater.* **2023**, 141, 105793.
 - 24 Xu, Z.; Cui, Y.; Li, T.; Dang, H.; Li, J.; Cheng, F. Enhanced mechanical and shape memory properties of poly(propylene

<https://doi.org/10.1007/s10118-025-3491-7>

- glycol)-based star-shaped polyurethane. *Macromol. Chem. Phys.* **2020**, *221*, 2000082.
- 25 Tian, W.; Xu, H.; Guo, Z.; Yu, H.; Shang, Y.; Tian, L. Polyurethane coatings modified by OH-PDMS for anti-cavitation, antifouling and anticorrosion applications. *Prog. Org. Coat.* **2023**, *179*, 107515.
 - 26 Wang, H.; Tang, N.; Zhang, R. Preparation and property controllability of dynamically crosslinked polyurethane modified bitumen. *Const. Build. Mater.* **2025**, *491*, 142700.
 - 27 Li, W.; Zuo, F.; Tian, W. A DA-bonded crosslinked epoxy-modified polyurethane elastomer with abrasion resistant, weathering resistant, corrosion-resistant, and self-healing functions. *Prog. Org. Coat.* **2025**, *208*, 109461.
 - 28 Nishiyama, Y.; Kumagai, S.; Motokucho, S.; Kameda, T.; Saito, Y.; Watanabe, A.; Nakatani, H.; Yoshiok, T. Temperature-dependent pyrolysis behavior of polyurethane elastomers with different hard-and soft-segment compositions. *J. Anal. Appl. Pyrol.* **2020**, *145*, 104754.
 - 29 Xing, Z.; Ding, C.; Wang, Z.; Yang, L.; Zhao, X.; Yang, X. The strengthening mechanism of mechanical performance for polyurethanes with micro-content crosslinkers. *Polymer* **2024**, *292*, 126574.
 - 30 Yilgör, E.; Yilgör, İ.; Yurtsever, E. Hydrogen bonding and polyurethane morphology. I. Quantum mechanical calculations of hydrogen bond energies and vibrational spectroscopy of model compounds. *Polymer* **2002**, *43*, 6551–6559.
 - 31 Wang, Y.; Yang, L.; Zhang, L.; Huang, H.; Qian, B.; Gu, S.; You, Z. Solvent-free synthesis of self-healable and recyclable crosslinked polyurethane based on dynamic oxime-urethane bonds. *Chinese J. Polym. Sci.* **2023**, *41*, 1725–1732.
 - 32 Yin, D.; Liu, Y.; Wang, X.; Hu, S.; Liu, L.; Zhao, X.; Zhang, L. Novel bio-based polyurethane elastomers for adjustable room-temperature damping property. *Compos. Commun.* **2024**, *49*, 101975.
 - 33 Jin, G.-Z.; Chen, L.-H.; Gong, Y.-Z.; Li, P.; Wang, R.-G.; Li, F.-Z.; Lu, Y.-L. Impact of hard segment structures on fatigue threshold of casting polyurethane using cutting method. *Chinese J. Polym. Sci.* **2025**, *43*, 303–315.
 - 34 Yin, D.; Zhai, M.; Wang, X.; Hu, S.; Zhao, X. Fully bio-based thermoplastic polyurethane composites with enhanced flame retardancy via phytic acid integration. *Mater. Today Commun.* **2025**, *45*, 112348.
 - 35 Wang, M.; Gao, H.; Jiang, J.; Gao, L.; Hu, G. Relationship between degree of microphase separation, crosslinking density, and anticorrosive performance of casting polyurethane coatings. *J. Coat. Technol. Res.* **2024**, *22*, 281–297.
 - 36 Sáenz-Pérez, M.; Laza, J. M.; García-Barrasa, J.; Vilas, J. L.; León, L. M. Influence of the soft segment nature on the thermomechanical behavior of shape memory polyurethanes. *Polym. Eng. Sci.* **2018**, *58*, 238–244.