

· 亮点评述 ·

当可逆交联弹性体遇到碳纤维：具有优异抗撕裂性能的柔性可回收复合材料

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摘要 兼具高柔性、优异抗撕裂性能的可回收碳纤维增强聚合物复合材料(CFRPs)的制备需依赖于具有高能量耗散能力的弹性体黏合剂的设计。满足这一需求的弹性体应集成高黏附性、低弹性模量、高力学强度、高韧性和高抗撕裂能力。然而，制备这种弹性体面临巨大挑战，因为这些性能之间通常是相互排斥的。最近，孙俊奇等设计了“多层级超分子作用力”，并以其聚集形成的微相结构交联高柔性的聚四氢呋喃链段，成功制备了断裂强度达83 MPa，韧性达619 MJ·m⁻³，断裂能达357 kJ·m⁻²，但模量仅为5.6 MPa的弹性体黏合剂。将该弹性体黏合剂和碳纤维布复合制备的碳纤维/弹性体复合材料具有高达767 MPa的断裂强度和创纪录的断裂能(2012 kJ·m⁻²)。该复合材料还具备修复缺陷和解离回收碳纤维布和弹性体的性能。

关键词 可逆交联弹性体，碳纤维增强聚合物复合材料，抗撕裂材料，可回收聚合物

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碳纤维增强聚合物复合材料(CFRPs)由聚合物黏合剂和碳纤维复合而成，具备轻质和高强度的特点。CFRPs在交通运输、装备制造、安全防护、风力发电和航空航天等领域发挥着关键作用，其产量持续增长，已成为重要的战略材料。目前，CFRPs通常由碳纤维布和环氧树脂等热固性塑料复合而成。这些热固性塑料固定了碳纤维的取向结构，使CFRPs具备高的强度和刚性，但也使其缺乏柔性，并且抗撕裂能力不足。因此，现有CFRPs难以满足软体机器人、个人防护设备和高空运载气球等新兴领域对柔性高强度碳纤维复合材料的需求。此外，热固性塑料黏合剂使CFRPs难以拆解和回收，导致资源浪费和环境污染。为此，亟需开发可回收的柔性弹性体

基黏合剂，将其与碳纤维复合，以制备抗撕裂且可循环利用的柔性高性能复合材料。

要赋予CFRPs优异的抗撕裂能力，弹性体黏合剂应该与碳纤维具有高黏附力，同时具备低模量和高能量耗散能力，以保证应力在CFRPs中的大面积传导和高效耗散^[1]。此外，弹性体黏合剂还需具备高力学强度和韧性，以提高柔性CFRPs的力学强度。然而，在同一弹性体体系中，实现高黏附性、低弹性模量、高力学强度、高韧性和高抗撕裂能力面临巨大挑战，因为弹性体的这些性能是相互排斥的。孙俊奇课题组提出并系统发展了原位生成微相分离结构与可逆作用力协同交联构筑高性能可逆交联弹性体的方法^[2,3]。最近，孙俊奇等利用高结合能的“多层级

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超分子作用力”将高柔性的聚四氢呋喃(PTMG)短链交联,成功制备了一种兼具低模量、高强度、高韧性和高撕裂能的可逆交联聚氨酯弹性体(PU)黏合剂^[4]。“多层次超分子作用力”由1个联吡啶-锌离子配位键和6对氨基甲酸酯氢键共同构成,其结合能高达 $67.3 \text{ kJ} \cdot \text{mol}^{-1}$. 在PU弹性体黏合剂中,这些“多层次超分子作用力”通过聚集形成硬而韧的微相结构,并将PTMG链段交联,使得PU的断裂强度达到83 MPa,韧性高达 $619 \text{ MJ} \cdot \text{m}^{-3}$. 同时,由于PTMG链段的高柔性,

PU的杨氏模量仅为5.6 MPa(图1(d)和1(e)). 在PU遭受<100%形变时,微相分离结构能够保持其完整性,从而使PU表现出高弹性和极低的滞后性能. 然而,当形变超过100%时,内部的“多层次超分子作用力”会随形变增加而逐步分离,导致微相结构发生变形直至瓦解,这一过程可高效耗散能量,使弹性体表现出高韧性和卓越的抗撕裂能力. 弹性体的断裂能高达 $357 \text{ kJ} \cdot \text{m}^{-2}$, 为已报道的弹性体的最高水平(图1(f)~1(h)).

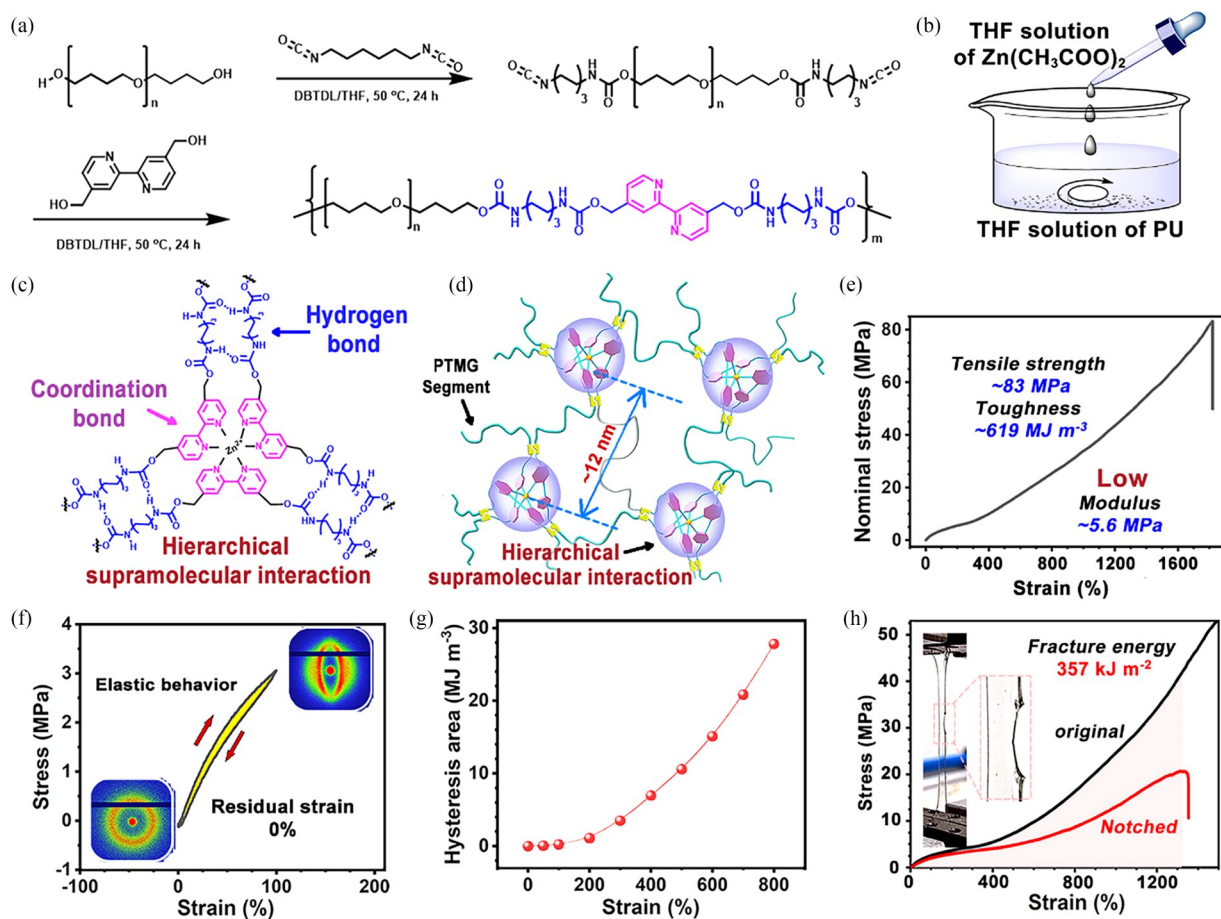


Fig. 1 (a) Synthesis routes of PU. (b) Schematic illustration of the preparation of PU elastomer binders. (c) Proposed structure of the hierarchical supramolecular interaction. (d) Schematic illustration of the structure of the PU elastomers. (e) Typical stress-strain curve of the PU elastomers. (f) The loading-unloading curves of the PU elastomers stretched to 100% strains. Inset images show 2D-SAXS patterns of the PU elastomers at 100% strains. (g) Hysteresis area of the PU elastomers as a function of strains. (h) Typical stress-strain curves of the intact and single-edge-notched PU elastomers. The inset image is the single-edge-notched elastomer at ~800% strain. (Reprinted with permission from Ref.[4]; Copyright (2024) Wiley-VCH).

将PU黏合剂的乙醇溶液刷涂在T300级碳纤维布表面,待溶剂挥发后,即可制备单层柔性CFRP(PU-CF). 由于PU中的氨基甲酸酯基团能与碳纤维表面的含氧基团形成氢键,PU能够牢固地黏附在碳纤维表面. 将单层PU-CF堆叠,再经

热压处理,可以制备多层PU-CF(记为PU-CF_x,其中 x 代表纤维布的层数). PU-CF中PU的含量为35 wt%,其断裂强度和韧性分别达到767 MPa和 $64.9 \text{ MJ} \cdot \text{m}^{-3}$,相较于裸碳纤维布的相应指标提升了超过2倍,充分证明了碳纤维与PU弹性体

黏合剂间存在强的黏合力(图2(a)). PU-CF 具有优异的抗穿刺能力和创纪录的抗撕裂能力, 其穿刺力和抗撕裂能分别高达 52.9 N 和 $1212 \text{ kJ} \cdot \text{m}^{-2}$ (图2(b)). PU-CF 卓越的力学强度和抗撕裂能力源于 PU 的高效能量耗散能力, 其原理如图2(c)所示: 当 PU-CF 遭受撕裂时, 低模量的 PU 会发生显著变形, 将撕裂力分散到更大面积的复合材料中, 从而避免裂口处的应力集中(图2(c)中图(i)); 随着撕裂力的增加, PU 的变形进一步加剧, 同时其内部的“多层级超分子作用力”逐步解离, 高效耗散撕裂力(图2(c)中图(ii)); 在极限撕裂力作用下, PU 与碳纤维之间的牢固黏附确保了碳纤

维以成股方式断裂, 而不是从复合材料中脱离抽出和单根断裂(图2(c)中图(iii)). 因此, 复合材料中的每根纤维都能充分发挥抵御损伤的能力; 同时, 裂口顶端的 PU 黏合剂也表现出卓越的抗撕裂性能. 这些因素共同作用, 赋予 PU-CF 复合材料优异的抗撕裂能力. 基于“多层级超分子作用力”以及聚氨酯(PU)与碳纤维(CF)之间氢键的动态可逆性, PU-CF 复合材料可以通过热压修复缺陷. 同时, 利用这种动态可逆性, PU-CF 复合材料在乙醇中浸泡后解离, 进而实现碳纤维和 PU 的无损回收(图2(d)和2(e)).

这种利用可逆交联弹性体作为黏合剂来制备

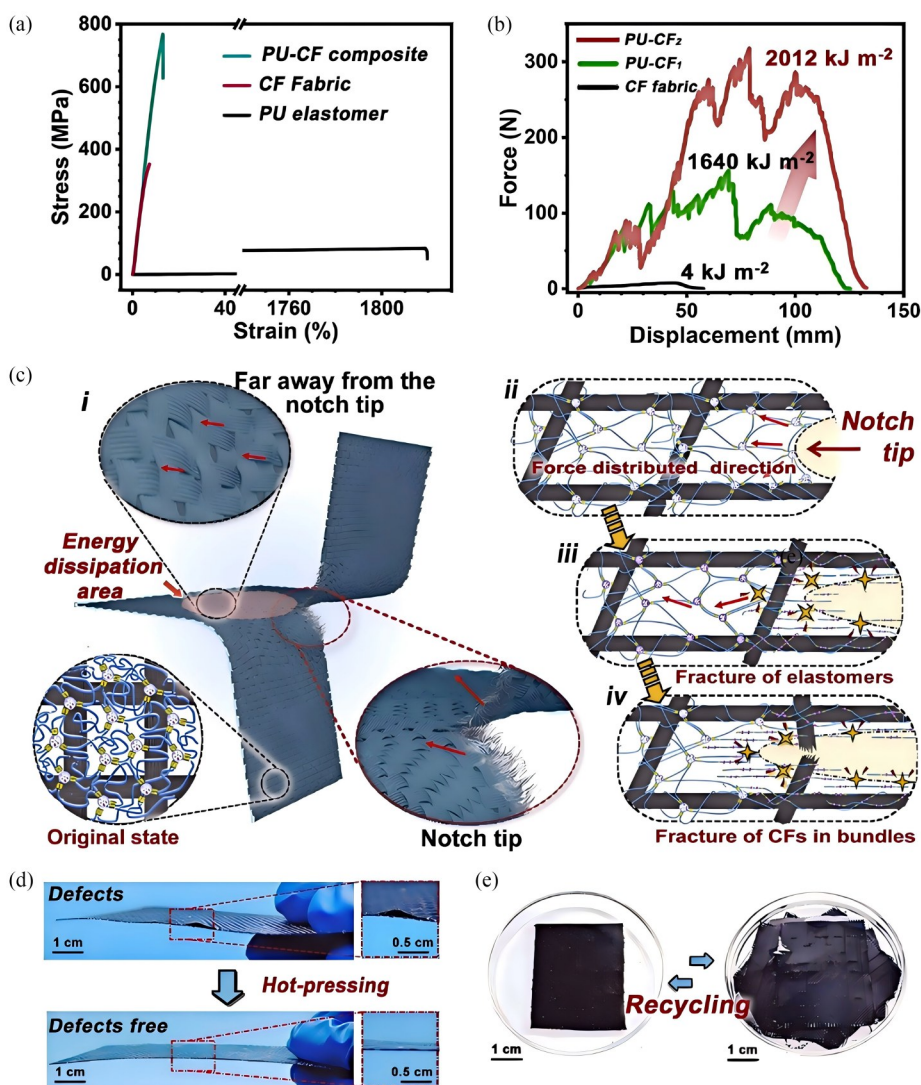


Fig. 2 (a) Typical stress-strain curves of the PU-CF composite, the CF fabric, and the PU elastomer. (b) The curves of tearing force as a function of displacement for CF fabric, PU-CF₁ and PU-CF₂ composites. (c) Proposed mechanism for the excellent tearing resistance of the PU-CF composites. The schematic illustration in (i) depicts the morphology of the PU-CF composite during tearing, while illustrations in (ii, iii, and iv) demonstrate the propagation process of a notch in the PU-CF composite. (d) Defects healing process for the PU-CF composites. (e) Recycling process of the PU-CF composites under the assistance of ethanol. (Reprinted with permission from Ref.[4]; Copyright (2024) Wiley-VCH).

柔性CFRPs的方法, 为高性能柔性复合材料的设计与制备提供了全新的思路. 柔性CFRPs的开发不仅丰富了复合材料的种类, 还拓展了其应用

领域. 此外, 这种制备柔性CFRPs的方法具有在凯夫拉纤维、玻璃纤维等高性能纤维基复合材料制备领域广泛推广的潜力.

REFERENCES

- 1 Cui, W.; King, D. R.; Huang, Y. W.; Chen, L.; Sun, T. L.; Guo, Y. Z.; Saruwatari, Y.; Hui, C. Y.; Kurokawa, T.; Gong, J. P. Fiber-reinforced viscoelastomers show extraordinary crack resistance that exceeds metals. *Adv. Mater.*, **2020**, 32(31), 1907180.
- 2 Wang, X. H.; Zhan, S. N.; Lu, Z. Y.; Li, J.; Yang, X.; Qiao, Y. N.; Men, Y. F.; Sun, J. Q. Healable, recyclable, and mechanically tough polyurethane elastomers with exceptional damage tolerance. *Adv. Mater.*, **2020**, 32(50), 2005759.
- 3 Guo, Z. W.; Lu, X. Y.; Wang, X. H.; Li, X.; Li, J.; Sun, J. Q. Engineering of chain rigidity and hydrogen bond cross-linking toward ultra-strong, healable, recyclable, and water-resistant elastomers. *Adv. Mater.*, **2023**, 35(21), 2300286.
- 4 Wang, X. H.; Sun, J. Q. Engineering of reversibly cross-linked elastomers toward flexible and recyclable elastomer/carbon fiber composites with extraordinary tearing resistance. *Adv. Mater.*, **2024**, 36(35), 2406252.

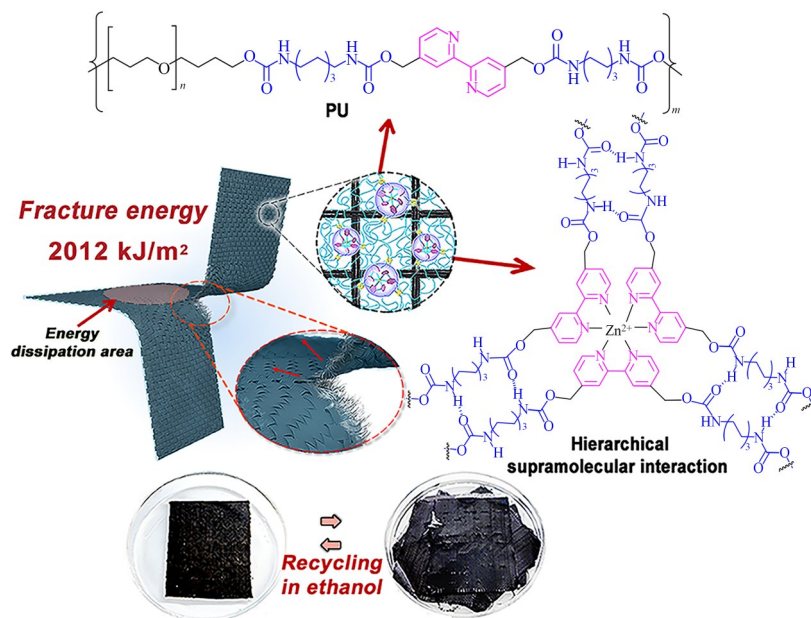
Highlight

When Reversibly Cross-linked Elastomers Meet Carbon Fibers: Flexible and Recyclable Composite Materials with Excellent Tearing Resistance

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Abstract The fabrication of recyclable carbon fiber-reinforced polymer composites (CFRPs) with high flexibility and excellent tearing resistance relies on the performance of the elastomer adhesives. To meet these requirements,



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the elastomers should possess high adhesion, low Young's modulus, high mechanical strength, toughness, and outstanding tearing resistance. However, achieving such a combination in a single elastomer is highly challenging, as these properties are often mutually exclusive. Recently, Junqi Sun *et al.* at Jilin University successfully fabricated an elastomer adhesive by physically crosslinking polytetrahydrofuran-based polyurethane (PU) chains with in situ-formed nanodomains composed of hierarchical supramolecular interactions of hydrogen and coordination bonds. This elastomer adhesive exhibits a tensile strength of 83 MPa, toughness of $619 \text{ MJ}\cdot\text{m}^{-3}$, fracture energy of $357 \text{ kJ}\cdot\text{m}^{-2}$, and a low modulus of 5.6 MPa. The carbon fiber/elastomer composite materials prepared using this elastomer adhesive exhibit a high tensile strength of 767 MPa and a record-high fracture energy of $2012 \text{ kJ}\cdot\text{m}^{-2}$. Moreover, these composites can heal defects when heated and be recycled through the dissociation of the PU elastomer adhesives.

Keywords Reversibly crosslinked elastomers, Carbon fiber-reinforced polymer composites, Tearing resistant materials, Recyclable polymers