Preparation of Polyurethane and Its Influence on the Properties of Epoxy System

Hanyi Duan

Guangdong Huangpu Institute of Materials, Guangzhou 510700, Guangdong, China

Abstract: ***To improve the toughness of epoxy resin curing system, a hydroxyl-terminated polyurethane (HTPU) toughener was synthesized from polyethylene glycol (PEG) and isophorone diisocyanate (IPDI), and its chemical structure was confirmed by FTIR and H-NMR. The toughener was added to bisphenol A epoxy resin/anhydride system with different mass fractions, and the thermomechanical properties and mechanical properties of the composites were systematically studied. The results show that: with the increase of the addition amount of HTPU toughener, the shear strength and elongation at break of the composites are both significantly improved. When the addition amount is 30%, the elongation at break can be increased by 275% and the shear strength is increased by 49.7%, indicating that its toughness and anti-cracking performance are effectively improved; at the same time, the tensile strength, storage modulus and glass transition temperature*** (T_g) ***all show a controllable decrease. The evolution law of this macroscopic property is due to the chemical bonding of the flexible long-chain of PU in the epoxy network, successfully constructing a rigid-flexible phase separation structure.***

Keywords: Epoxy resin; Polyurethane; Toughening; Mechanical properties.

1. INTRODUCTION

Epoxy resin occupies an important position in technical fields such as aerospace, electronic packaging, composites, and adhesives due to its excellent mechanical properties, outstanding adhesive strength, high chemical stability, and convenient processing technology. However, after curing and crosslinking, epoxy resin forms a dense three-dimensional network structure, which, while endowing it with high stiffness and strength, also results in inherent brittleness. This limits its application in harsh environments that require high reliability and fatigue resistance. Therefore, improving the toughness of epoxy resin has always been a research hotspot and difficulty in the field of polymer materials.

To overcome the brittleness problem of epoxy resin, researchers have developed various toughening technologies. Traditional methods mainly include toughening with rubber elastomers (such as carboxyl-terminated nitrile rubber), toughening with thermoplastic resins (such as polyethersulfone, polyetherimide, etc.), toughening with nanoparticles (nano-silica, carbon nanotubes, graphene, etc.), and toughening with flexible chain segments. Toughening with rubber elastomers dissipates energy and improves toughness by forming a phase-separated "sea-island" structure and inducing crazes, shear bands, etc. in rubber particles. Thermoplastic resins can form a co-continuous or inverse phase structure. Rutherford et al. (2026) conducted measurements and modeling to investigate GUV222-driven increases in secondary organic aerosol (SOA) concentrations in an unoccupied office, revealing that such ultraviolet irradiation could promote SOA formation under indoor conditions [1]. Similarly, Narouei et al. (2025) examined the effects of germicidal far-UVC on ozone and particulate matter in a conference room, finding that far-UVC exposure can alter ozone levels and particulate dynamics, which has implications for indoor air quality [2]. In a different domain, Sun (2024) focused on microbial biotechnology by modifying and screening antibiotic-producing strains, demonstrating effective strategies to enhance antibiotic yield through strain improvement [3]. Meanwhile, Wu et al. (2025) prepared a Pd/Ni bimetallic catalyst and applied it to the selective hydrogenation of phenol, achieving high activity and selectivity that could benefit catalytic hydrogenation processes [4]. Finally, Xiao et al. (2022) developed an ultrasmall Fe_3O_4-decorated polydopamine hybrid nanozyme that enables continuous conversion of oxygen into toxic hydroxyl radicals via glutathione-depleted cascade redox reactions, and they demonstrated its intensive wound disinfection capability [5].

Among many strategies, polyurethane toughening has attracted much attention due to the flexibility of its design, excellent toughening effect, good compatibility and reactivity with epoxy. Polyurethane is a block copolymer formed by the alternation of soft segments/flexible chain segments (usually polyether or polyester polyols) and hard segments (formed by the reaction of diisocyanate with small molecule chain extenders) through microphase separation [6]. This structure with alternating hard and soft segments endows PU with excellent mechanical properties: the soft segments provide elasticity and toughness, the hard segments provide strength and modulus,

and energy is dissipated through the stretching and slipping of molecular chains.

There have been many studies on the modification of epoxy systems with polyurethanes synthesized from different types of isocyanates and polyols, and the changes in the mechanical properties and thermal stability of the systems and the toughening mechanism have been investigated [7-14]. Sun Tao et al. [15] synthesized poly(ethylene glycol)-type amino-terminated polyurethanes with different number-average molecular weights and used them in bisphenol A-type epoxy resin systems, and found that their flexibility was improved but the adhesion was reduced. It has also been found that hydroxy aliphatic polyesters can improve the fracture toughness more than amine- or acid-terminated polyesters, which may be due to the effective increase in molecular weight through chain extension reactions [16]. Kostrzewa et al. [17] prepared polyurethanes using MDI and PEG and poly(propylene glycol) (POPD) with different molecular weights as raw materials. The results showed that polyurethanes with an excess of isocyanate groups were added to the epoxy resin, forming a graft interpenetrating polymer network structure. At the same time, it was observed that polyurethanes synthesized from higher molecular weight POPD exhibited higher impact strength, while polyurethanes prepared from PEG had higher flexural fracture energy and higher flexural modulus.

As a polyether polyol with strong hydrophilicity and good flexibility, polyethylene glycol is an ideal choice for constructing the soft segment of PU. Isophorone diisocyanate, as an alicyclic diisocyanate, usually has excellent light stability and mechanical properties, and its reactivity and spatial structure may have an important impact on the compatibility and phase separation behavior of PU and EP. A hydroxyl-terminated polyurethane prepolymer with polyethylene glycol as the soft segment and isophorone diisocyanate as the hard segment was designed and synthesized, and it was applied to the epoxy resin/anhydride system to study its heat resistance and mechanical properties.

2. EXPERIMENTAL SECTION

2.1 Main Raw Materials

Polyethylene glycol PEG400: PETRONAS; Polyethylene glycol PEG600: PETRONAS; Isophorone diisocyanate IPDI: Wanhua Chemical; Catalyst: self-prepared, 1% mass fraction of dibutyltin dilaurate - polytetrahydrofuran solution; Bisphenol A epoxy resin DEGBA: 0164, Nantong Xingchen Synthetic Materials Co., Ltd.; Methylhexahydrophthalic anhydride (MHHPA): AMH-850, Zhejiang Alpha Chemical Technology Co., Ltd.; 2, 4, 6-Tris(dimethylaminomethyl)phenol: DMP-30, Chuzhou Huisheng Electronic Materials Co., Ltd.

2.2 Preparation of PU Toughening Agent

The raw materials were dehydrated with molecular sieves in advance. Weigh 100 g PEG600 into a three-neck flask, add the catalyst solution, weigh 98 g IPDI into a constant pressure dropping funnel, slowly drop it into the three-neck flask, react for 3 h, then add 7. 5 g PEG400, and finally react at 80°C for 10 h to obtain a light yellow viscous liquid, which is hydroxyl-terminated polyurethane (HTPU).

2.3 Preparation of Epoxy Adhesive

(1) Preparation of adhesive solution: First, preheat the prepared HTPU to 60 °C for easy取用. Weigh the corresponding masses of each component according to the formula in Table 1, add them in sequence, manually stir after adding each component until the components are preliminarily mixed, then put them into a homogenizer and stir at 1600 r/min for 3 min while evacuating, and finally obtain a uniformly mixed adhesive solution.

(2) Preparation of specimens: Pour the prepared adhesive solution into a flat tetrafluoroethylene mold that meets the test national standard. The mold needs to be pre-coated with silicone grease, pour it slowly to avoid entraining air bubbles, put it into a vacuum drying oven to defoam until no air bubbles emerge on the surface, and then put it into a forced-air oven for curing. The curing process is 125 °C/1 h + 170 °C/3 h. After curing, cool it naturally to room temperature, and take out the test specimens that meet the national standard size.

Table 1: Experimental formula of EP/MHHPA system Unit: g

Raw materials	Formulation				
	1	2	3	4	5
DEGBA	100	95	90	80	70
HTPU		5	10	20	30
MHHPA	91	87	82	76	66.5
DMP-30	0.5	0.48	0.45	0.42	0.37

2.4 Main Instruments and Characterization Tests

Blast drying oven: DHG-9053A, Shanghai Yiheng Scientific Instrument Co., Ltd.; Vacuum drying oven: DZF-6053, Shanghai Yiheng Scientific Instrument Co., Ltd.; Homogenizer: ZYMC-350VS, Shenzhen Zhongyi Technology Co., Ltd.

Nuclear Magnetic Resonance Spectrometer (NMR): The JNM-ECZ400S Nuclear Magnetic Resonance Spectrometer produced by JEOL Ltd. of Japan was used. Deuterated DMS0 was used as the solvent, and the number of scans was 16 times.

Fourier transform infrared spectrometer (FTIR): The VERTEX 70v infrared spectrometer from Bruker, Germany was used. The sample was prepared by the potassium bromide tablet pressing method. The scanning range was $4000 \sim 400\ \mathrm{cm}^{-1}$, the number of scans was 32, and the resolution was $4\ \mathrm{cm}^{-1}$.

Differential Scanning Calorimeter (DSC): The test was carried out using a DSC25 differential scanning calorimeter from TA Instruments, USA, with a temperature range of $25 \sim 250°\mathrm{C}$, a heating rate of $3°\mathrm{C/min}$, and a nitrogen atmosphere.

Dynamic mechanical analyzer (DMA): The test was carried out using a DMA850 dynamic mechanical analyzer from TA Instruments, USA. The temperature range was 25 - 165 °C, and the heating rate was 3 °C/min.

Shear and tensile property tests: The tests were carried out using a German ZwickRoell high and low temperature electronic universal material testing machine in accordance with GB/T 7124-2008 Adhesives - Determination of tensile shear strength (rigid-to-rigid) and GB/T 1040.1—2025 Plastics - Determination of tensile properties - Part 1: General principles.

3. RESULTS AND DISCUSSION

3.1 HTPU Structure

After the reaction of IPDI and PEG, a polyurethane product is formed. The reaction equation is: -NCO + -OH → -NH-CO-O-. Assuming complete reaction, all isocyanate and hydroxyl groups participate in the reaction. The infrared spectrum and proton nuclear magnetic resonance spectrum of the product are shown in Figures 1 and 2.

As can be seen from Figure 1, the asymmetric stretching vibration absorption peak at $2261\ \mathrm{cm}^{-1}$ of $-\mathrm{NC0}$ completely disappears in the product, and the stretching vibration absorption peak at $3400\ \mathrm{cm}^{-1}$ of $0-\mathrm{H}$ weakens significantly, indicating that the -NCO in IPDI and $-0\mathrm{H}$ in PEG are consumed. Moreover, strong peaks that do not appear in IPDI and PEG appear at $1715\ \mathrm{cm}^{-1}$ and $3318\ \mathrm{cm}^{-1}$, which are the stretching vibration absorption peak of C=O in urethane and the stretching vibration absorption peak of secondary amide $N-H$ respectively. In summary, it can be judged that the product with the expected structure is synthesized.

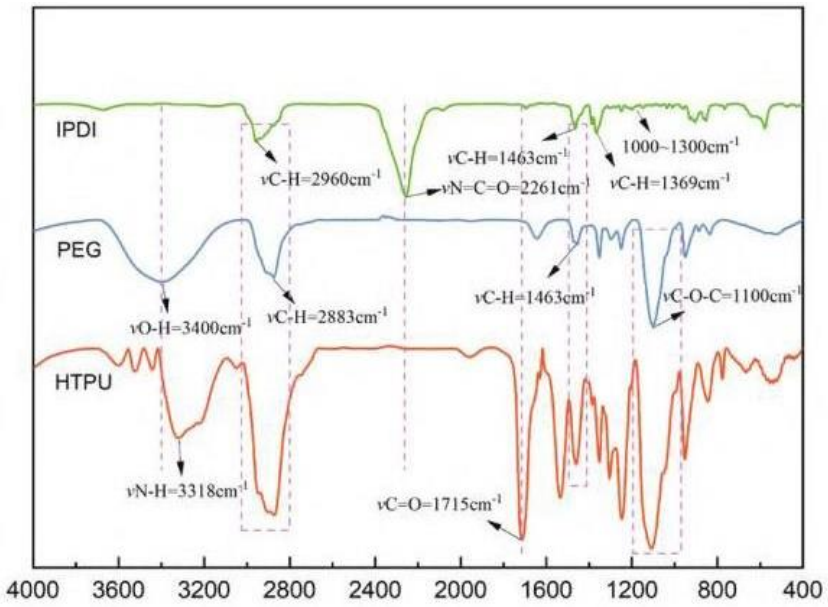


Figure 1: Infrared Spectrum of the Product

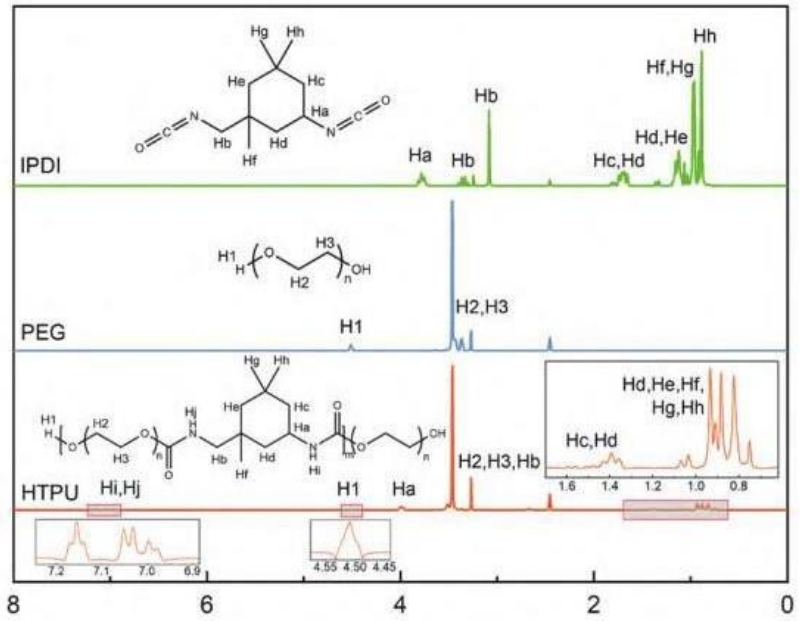


Figure 2: HNMR Spectrum of the Product

The product is detected by proton nuclear magnetic resonance spectrum. As shown in Figure 2, the signal of the hydroxyl hydrogen at the end of PEG near 4.55ppm weakens because the hydroxyl group is consumed in the reaction. However, due to PEG capping, there are still terminal hydroxyl groups. A new broad peak appears in the range of 7.0 ~ 7.15ppm for HTPU, corresponding to the -NH-hydrogen in the urethane group, indicating the formation of polyurethane bonds. In addition, the strong singlet of the backbone methylene hydrogen (-O-CH_2-CH_2-O-)) in the PEG part still appears near 3.51 ppm; the methyl hydrogen ($-CH_3$) on IPDI in the multiplet in the range of 0.8 ~ 1.0ppm, and the multiplets of the methylene and methane hydrogens ($-CH_2-/-CH-$) on the ring in the range of 1.08 ~ 1.85ppm are still retained. The methane hydrogen originally connected to NC0 in IPDI moves to around 3.98 ppm in chemical shift due to the electron-withdrawing effect of urethane after the reaction. In summary, the results of NMR further indicate that the compound with the expected structure is successfully prepared.

3.2 Non-isothermal DSC Test Analysis

The non-isothermal DSC curves of the system at 3 °C/min when the HTPU content is 0%, 10%, 20%, and 30%

are shown in Figure 3.

As can be seen from Figure 3: With the increase of the HTPU content, the position of the curing peak of the system shifts slightly to the right from 116.67 - 163.20 °C to 119.54 - 165.85 °C, and the heat of exotherm decreases significantly. The heat of exotherm of the un-toughened system is 318.66 J/g. When the HTPU content is increased to 30%, the heat of exotherm of the system decreases by 29.7%. This may be because the reaction between epoxy and anhydride is a highly exothermic reaction, and there are two possible reaction paths for the terminal hydroxyl groups in HTPU: one is the reaction between the terminal hydroxyl group and the anhydride, and the other is the direct reaction between the terminal hydroxyl group and the epoxy group under the catalysis of DMP-30. The heat release of both reactions is lower than that of the epoxy-anhydride reaction. The addition of HTPU causes the hydroxyl groups to "seize" a part of the opportunity for the highly exothermic epoxy-anhydride reaction and converts it into a reaction with lower heat release. In addition, the introduction of the polyurethane long chain, integrated as a flexible segment into the network, may reduce the final crosslinking density of the system. The reduction of crosslinking points also means a decrease in highly exothermic reaction events. Therefore, the heat of exotherm shows a significant decrease.

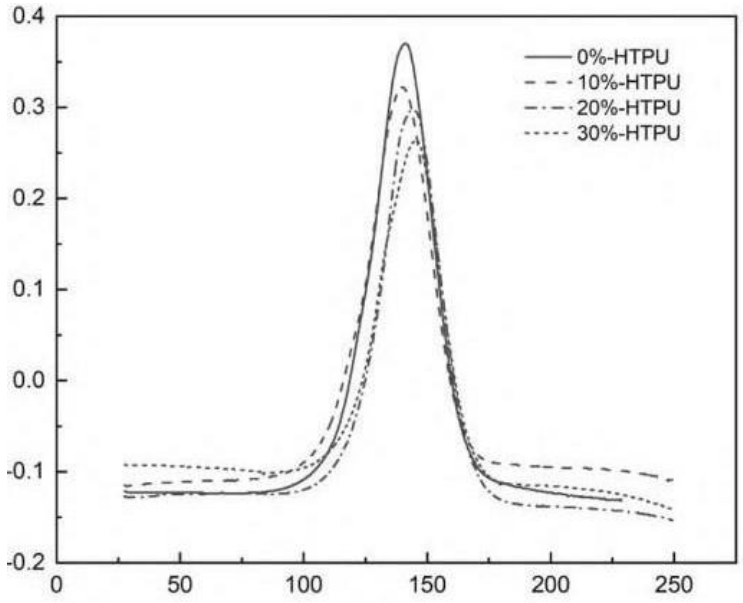


Figure 3: Non-isothermal DSC curves of the epoxy system at different HTPU contents

Table 2: DSC parameters of the cured system at different HTPU contents

HTPU addition amount / %	T_i/C	T_p/°C	T_f/°C	ΔH_0/(J/g)
0	116.67	141.07	163.20	318.66
10	115.15	139.77	162.47	272.24
20	122.07	144.42	165.38	258.97
30	119.54	145.49	165.85	224.11

3.3 DMA Test Analysis

The variations of storage modulus and Tan δ with temperature at different HTPU addition amounts are shown in Figures 4 and 5. First, as the HTPU addition amount increases, the glass transition temperature of the system decreases from 151.16 °C without toughening to 120.19 °C with 30% toughening component added, and the retention rate of the storage modulus also decreases with the increase in the addition amount. Since the synthesized HTPU is essentially polyurethane, its T_g and modulus are lower than those of epoxy resin. The introduction of the PEG flexible segment macroscopically plays a role in "diluting" the rigid epoxy network, making the network more flexible, increasing the length and mobility of the segments between crosslinking points, and enabling the entire network segments to undergo cooperative motion at lower temperatures. In addition, the peak value of the Tan δ curve decreases and the peak width broadens. The broadening of the peak usually means that there is a wide interfacial phase at the interface between the PU and EP phases. The epoxy segments in this interfacial phase are activated by the adjacent PU flexible chains. As the addition amount increases, the formation and relaxation process of its phase separation structure occur in a wider temperature range, which is a typical feature of

toughening.

T_g and the decrease in storage modulus are not simply performance deterioration but direct evidence of the successful transformation of the material from a homogeneous rigid network to a rigid-flexible multiphase network, which is a typical structural feature accompanying effective toughening. This significant improvement in toughness achieved by sacrificing controllable stiffness has important value in application scenarios that require high crack resistance and impact resistance.

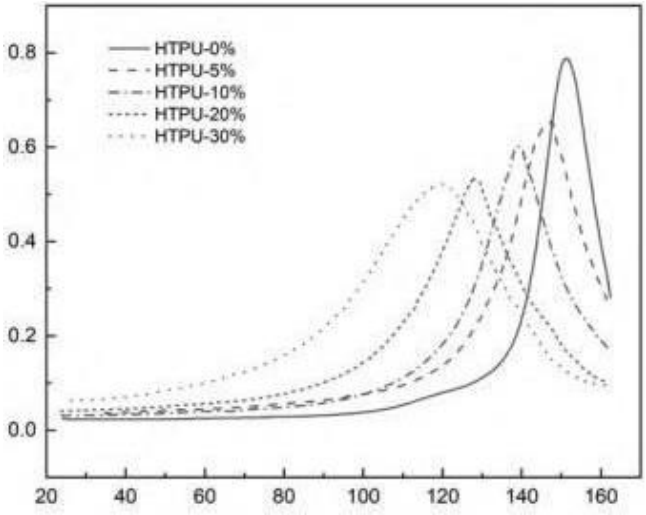


Figure 4: Curve of Tan δ Variation with Temperature at Different HTPU Addition Amounts

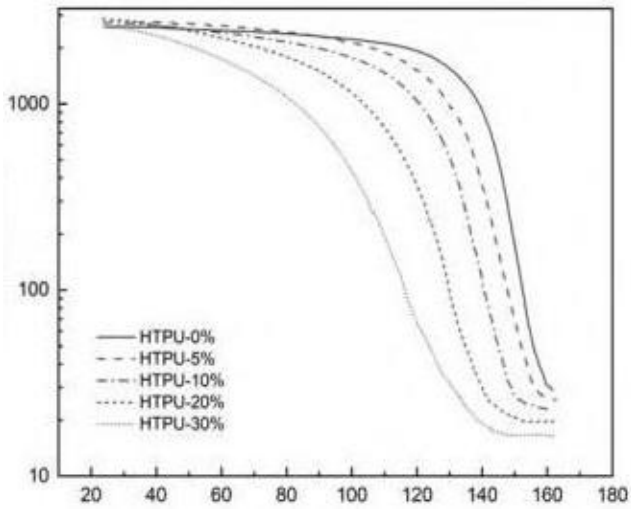


Figure 5: Curve of Storage Modulus Variation with Temperature at Different HTPU Addition Amounts

3.4 Mechanical Property Analysis

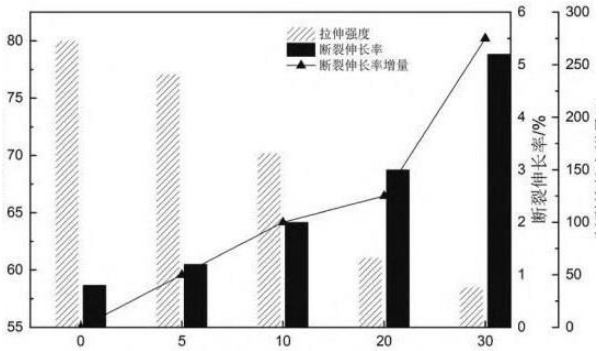


Figure 6: Influence of HTPU Addition Amount on Tensile Strength and Elongation at Break

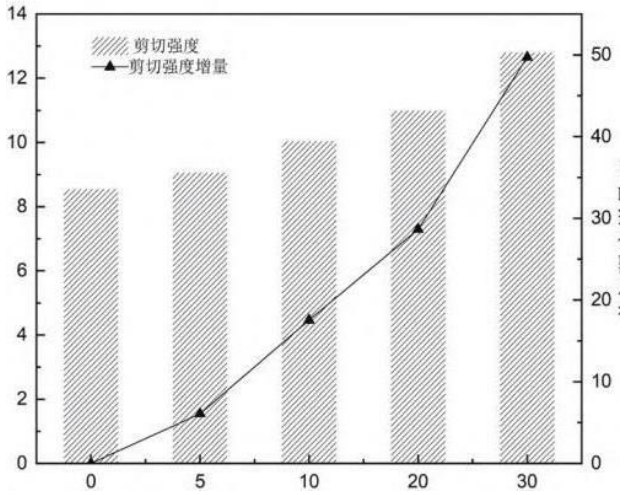


Figure 7: Influence of HTPU Addition Amount on Shear Strength

Figures 6 and 7 show the changes in tensile strength, elongation at break, and shear strength with the addition amount of HTPU. It can be seen that as the addition amount increases, the tensile strength decreases and the elongation at break increases. When the addition amount increases to 30%, the elongation at break increases by 275%, and the tensile strength at this time is still 58.5 MPa. This shows that the flexible chain segments can undergo large deformations and absorb a large amount of energy under external forces, which is one of the direct evidences for the improvement of the toughness of the synthesized HTPU material. At the same time, it can be seen from the stress-strain curve in Figure 8 that after adding 20%, the curve begins to show a yield stage, indicating that the material is gradually changing from a brittle material to a ductile material. The shear strength also increases with the increase in the addition amount. When the addition amounts are 5%, 10%, 20%, and 30%, the shear strengths increase by 6.1%, 17.5%, 28.7%, and 49.7% respectively. This is because the flexible long chains of PU introduce more energy dissipation mechanisms and improve the interfacial stress distribution.

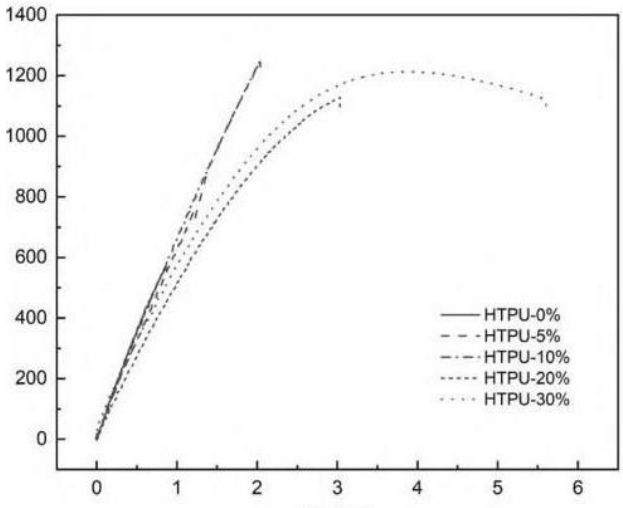
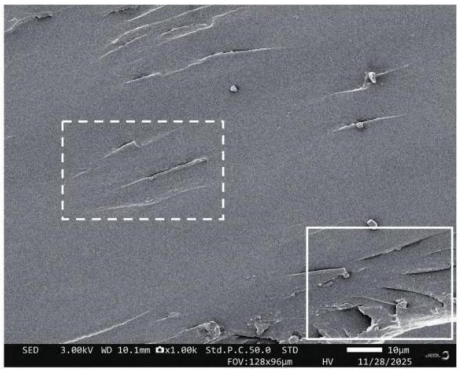


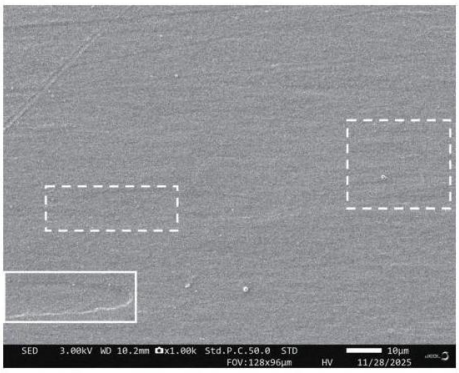
Figure 8: Stress-strain curve

The scanning electron microscope image of the tensile fracture surface of the cured product is shown in Figure 9. As can be seen from Figure 9 (a), for the sample without HTPU addition, the fracture surface is very smooth (mirror area), with clear river-like patterns (dashed box), sparse patterns, and the direction tends to be the same direction, that is, the crack propagation direction. In addition, clear and steep feather-like patterns (solid box) can be seen, and there is no obvious stress dispersion phenomenon, belonging to cleavage fracture, which is a typical brittle fracture characteristic. As can be seen from Figure 9 (b), for the epoxy resin cured product with 30% HTPU addition, the fracture surface is flat and smooth, the fracture boundary is blurred, the cracks are fine, there are obvious fine fringed micelle structures (dashed box), and shell-shaped arc dimples textures (solid box) appear. After further magnifying to 15000 times, as shown in Figure 9 (c), more obvious fringed bundle structures (dashed line) and scaly dimple structures (solid box) are observed, indicating that the yield stage is experienced during the

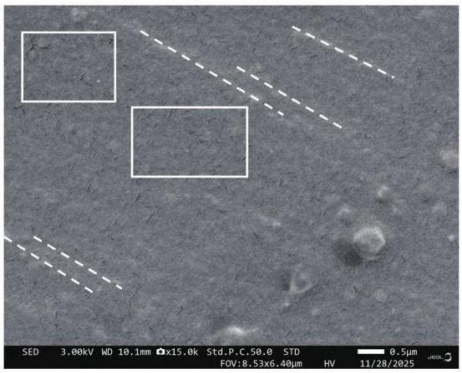
tensile process, which is an obvious characteristic of ductile fracture. It shows that when subjected to external forces, the flexible chain segments in HTPU can absorb energy, blunt cracks, and inhibit crack propagation, thereby improving the toughness of epoxy resin.



(a) SEM image of the fracture surface without HTPU addition, magnified 1000 times



(b) SEM image of the fracture surface with 30% HTPU addition, magnified 1000 times



(c) SEM image of the fracture surface with 30% HTPU addition, magnified 15,000 times

Figure 9: Scanning electron microscope images of the fracture surfaces of epoxy resin cured products

4. CONCLUSIONS

A hydroxyl-terminated polyurethane toughener was synthesized for the first time using a PEG600/PEG400 composite soft segment and IPDI, and the effects of the hydroxyl-terminated polyurethane toughener on the properties of epoxy resin composites were systematically investigated. The changes in their mechanical properties and thermomechanical properties showed a high degree of consistency, jointly revealing the successful toughening effect and its internal mechanism. The conclusions are as follows.

1) The results of DSC tests showed that the addition of this polyurethane toughener reduced the curing enthalpy of the system.

2) The results of DMA tests showed that this polyurethane had a toughening effect, but the glass transition

temperature decreased with the increase in the addition amount.

3) The results of mechanical property tests further showed that when the addition amount of this toughener was 30%, the elongation at break could be increased by 275% and the shear strength could be increased by 49.7%. However, due to the decrease in the glass transition temperature, the toughness and heat resistance need to be balanced during actual industrial use.

Toughening is an eternal topic in the application process of epoxy resins. This HTPU can significantly improve the elongation at break and shear strength, making it very suitable for fields with high requirements for impact resistance and crack resistance, such as flexible electronic packaging materials, which can protect internal brittle components from cracking under stress; high-performance structural adhesives, which can absorb stress through plastic deformation and greatly improve the durability and reliability of bonded joints. At the same time, the moderate modulus retention and controllable T_g of this system also make it valuable in fields such as composite material matrices that require a balance between toughness and certain stiffness.

FUNDING PROJECT:

Supported by the Science and Technology Plan Project of Guangzhou (202206070002).

REFERENCES

[1] Rutherford, M., Peng, Z., Jenks, O. J., Mesburis, R., Day, D., Handschy, A., ... & de Gouw, J. (2026). Measurements and Modeling of GUV222-Driven Increases in SOA Concentrations in an Unoccupied Office. ACS ES&T Air, 3(3), 875-886.

[2] Narouei, F. H., Tang, Z., Wang, S. I., Hashmi, R. H., Welch, D., Sethuraman, S., ... & McNeill, V. F. (2025). Effects of germicidal far-UVC on ozone and particulate matter in a conference room. Plos one, 20(8), e0328224.

[3] Sun, B. (2024). Modification and Screening of Antibiotic-producing Strains. Innovation & Technology Advances, 2(2), 21-33.

[4] Wu, Y., Xiaolu, Q., Liu, X., & Tian, H. (2025). Preparation of a Pd/Ni Bimetallic Catalyst and its Application in the Selective Hydrogenation of Phenol. Innovation & Technology Advances, 3(2), 1–18. https://doi.org/10.61187/ita.v3i2.209

[5] Xiao, J., Hai, L., Li, Y., Li, H., Gong, M., Wang, Z., ... & He, D. (2022). An Ultrasmall Fe3O4 ‐ Decorated Polydopamine Hybrid Nanozyme Enables Continuous Conversion of Oxygen into Toxic Hydroxyl Radical via GSH ‐ Depleted Cascade Redox Reactions for Intensive Wound Disinfection. Small, 18(9), 2105465.

[6] Ye Mu-yi, Chen Xun-jun, Guo Qing-bing, et al. Research progress on toughening and modification of epoxy resin [J]. New Chemical Materials, 2025, 53 (5): 30-35.

[7] CIOBANU C, HAN X, CASCAVAL C N, et al. Influence of urethane group on properties of crosslinked polyurethane elastomers [J]. Journal of Applied Polymer Science, 2010, 87: 1858-1867.

[8] DIACONU I, CIOBANU C, SIMIONESCU C I. Properties of urethane elastomers [J]. Polymer Bulletin, 1990, 24: 573-576.

[9] LEE J Y, SHIM M J, KIM S W. Effect of polyurethane toughening on the properties of epoxy resin[J]. Journal of Applied Polymer Science, 1998, 67 (6): 965-971.

[10] CRISTEA M, IBANESCU S, CASCAVAL C N, et al. Dynamic Mechanical Analysis of Polyurethane-Epoxy Interpenetrating Polymer Networks [J]. High Performance Polymers 2009, 21 (5): 608-623.

[11] PARK S J, JIN J S. Energetic studies on epoxy-polyurethane interpenetrating polymer networks [J]. Journal of Applied Polymer Science, 2001, 82 (3): 775-780.

[12] BAKAR M, DUK R, PRZYBYLEK M, et al. Mechanical and Thermal Properties of Epoxy Resin Modified with Polyurethane[J]. Journal of Reinforced Plastics and Composites, 2009, 28 (17): 2107-2118.

[13] WANG H H, CHEN J C. Toughening of epoxy resin by reacting with functional terminated-polyurethanes [J]. Journal of Applied Polymer Science, 1995, 57 (6): 671-677.

[14] PAN C Y, QI L W, LIU Y. Properties' improvement of epoxy resin using prepolymers prepared from diisocyanates and 3,9-dihydroxyethyl-3',9'-dibenzyl-1,5,7,11-tetraoxas-piro (5, 5) undecane[J]. European Polymer Journal, 1999, 35 (10): 1813 – 1819.

[15] ONG S, ISMAIL J, BAKAR M, et al. Polyurethane-modified epoxy resin: Solventless preparation and properties [J]. Journal of Applied Polymer Science, 2009, 111 (6): 3094-3103.

[16] Sun Tao, Guan Jianguo, Yu Jianying, et al. Study on synthesis of amino - terminated polyurethane and toughening of epoxy resin [J]. Polymer Materials Science and Engineering, 2005, 21 (1): 117 - 120+124.
[17] HARANI H, FELLAHI S, BAKAR M. Toughening of epoxy resin using synthesized polyurethane prepolymer based on hydroxyl-terminated polyesters [J]. Journal of Applied Polymer Science, 1998, 70: 2603-2618.
[18] KOSTRZEWA M, HAUSNEROVA B, BAKAR M, et al. Property evaluation and structure analysis of polyurethane/epoxy graft interpenetrating polymer networks[J]. Journal of Applied Polymer Science, 2011, 122: 1722-1730.

Author Profile

Hanyi Duan (1997-), female, Han nationality, master, research fields: epoxy resin adhesives and composites, etc.