

Supporting Information

Hyperbranched polyborate modified HTPB adhesives with enhanced performance and lower glass transition temperature

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Supplementary information S1

S 1.1 Reagents and materials

Tributyl borate (TBB, AR) and diethylene glycol (DEG, AR) were purchased from Shanghai Macklin Biochemical Co., Ltd. Toluene diisocyanate (TDI, AR) and methanol (99.5%) were also sourced from Shanghai Macklin Biochemical Co., Ltd. Dichloromethane (DCM, 99.5%) was obtained from Energy Chemical. Acetone (99.5%) was supplied by China National Pharmaceutical Group Chemical Reagent Co., Ltd. Anhydrous ethanol (AR) was purchased from Guangdong Guanghua Sci-Tech Co., Ltd. Hydroxyl-terminated polybutadiene (HTPB) was acquired from Tianyuan Aerospace Material (Yingkou) Technology Co., Ltd. All other glassware was provided by Xi'an Haotian Glass Instrument Co., Ltd.

S 1.2 Characterization

Fourier Transform Infrared Spectroscopy (FT-IR) measurements were conducted over the range of 400 cm^{-1} to 4000 cm^{-1} using a Nicolet FT-IR 5700 spectrometer (USA). The molecular weight and distribution were measured using Gel Permeation Chromatography (GPC, Waters 2414, USA) with tetrahydrofuran (THF) as the mobile phase. The GPC test employed eighteen-angle light scattering, utilizing an HPLC (High-Performance Liquid Chromatography) column. The test was conducted at a temperature of 40°C . According to GB/T 7383-2007 (Chinese standard), the concentration of -OH groups in HBPB was determined using the titration method. The crosslinking density was measured using a low-field Nuclear Magnetic Resonance analyzer (NIUMAG, PQ001, China). Tensile tests were conducted on a electro-mechanical universal testing machine (CMT 6303) at a tensile speed of $500\text{ mm}\cdot\text{min}^{-1}$ at room temperature, according to GB/T 528-2009 (Chinese standard), using Type 1 dumbbell-shaped specimens. The low-temperature mechanical properties were tested on a Shimadzu AG-X plus universal testing machine according to GB/T 528-2009 (Chinese standard) with a tensile speed of $500\text{ mm}\cdot\text{min}^{-1}$ and a test temperature of -40°C . The surface morphology of the material fracture surface was observed using a tungsten filament scanning electron microscope (SEM, TESCAN VEGA 3 LMH). The tensile shear strength of the adhesive was tested according to GB/T 7124-2008 (Chinese standard), with 6061 aluminum alloy as the test plate, dimensions of $100\text{ mm}\times 25\text{ mm}\times 1.5\text{ mm}$, and the bonding surface length of $12.5\text{ mm} \pm 0.25\text{ mm}$. Thermogravimetric analysis (TGA) was performed on a thermogravimetric analyzer (STA 449F3, Germany) under nitrogen atmosphere at a heating rate of $20^\circ\text{C}\cdot\text{min}^{-1}$ from 30°C to 800°C . Dynamic thermomechanical analysis (DMA) was tested by a Q800 dynamic thermomechanical analyzer (NETZSCH DMA 242E), adopting a tensile mode, with a heating rate of $3^\circ\text{C}\cdot\text{min}^{-1}$ from -100°C to 0°C and a frequency of 1 Hz. The sample size was $15\text{ mm}\times 5\text{ mm}\times 2\text{ mm}$.

Supplementary information S2

S 2.1 GPC result of HBPB

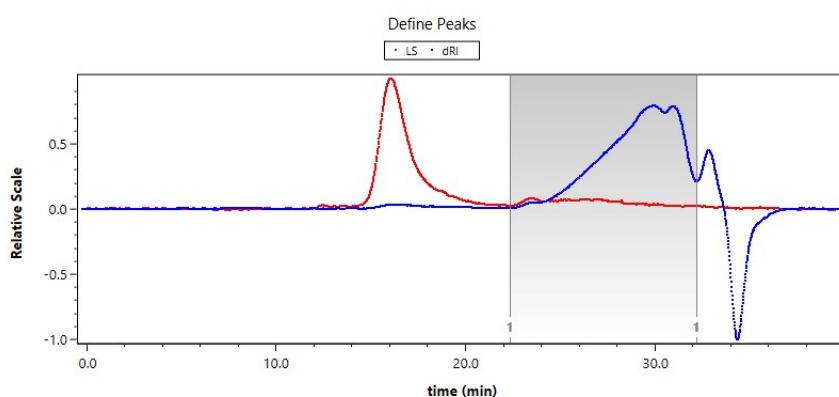


Figure S1 GPC curve of HBPB in THF

Table S1 Molecular weights and distributions of HBPB

Polymer	M_n	M_w	M_p	M_z	PDI (M_w/M_n)
HBPB	16500	24640	11600	75800	1.489

S 2.2 The concentration of -OH group in HBPB

The hydroxyl value of the hyperbranched polyborate ester was determined according to the national standard GB/T 7383-2007 “Determination of Hydroxyl Value of Nonionic Surfactants” using the phthalic anhydride method. Approximately 1.00 g of HBPB was weighed into a round-bottom flask and mixed with 25.0 mL of pyridine solution of phthalic anhydride (140 g \pm 1 g phthalic anhydride dissolved in 1 L pyridine). A condenser, pre-rinsed with pyridine, was connected to the flask. The flask was swirled to mix the contents, and then heated to reflux gently for 1 hour at a temperature of 115 \pm 2 $^{\circ}$ C. After reflux, the mixture was cooled to room temperature. Exactly 50.0 mL of 0.5 mol \cdot L $^{-1}$ NaOH standard solution was added using a burette, followed by the addition of 4-5 drops of phenolphthalein indicator (1 g phenolphthalein dissolved in 100 mL pyridine). The solution was titrated with the NaOH standard solution until a pink color persisted for 15 seconds as the endpoint. Three blank tests were conducted simultaneously. The hydroxyl value $I_{(OH)}$ (mol \cdot g $^{-1}$) of the sample was calculated using equation (1).

$$I_{(OH)} = \frac{c \times (V_0 - V_1)}{m_0} \quad (1)$$

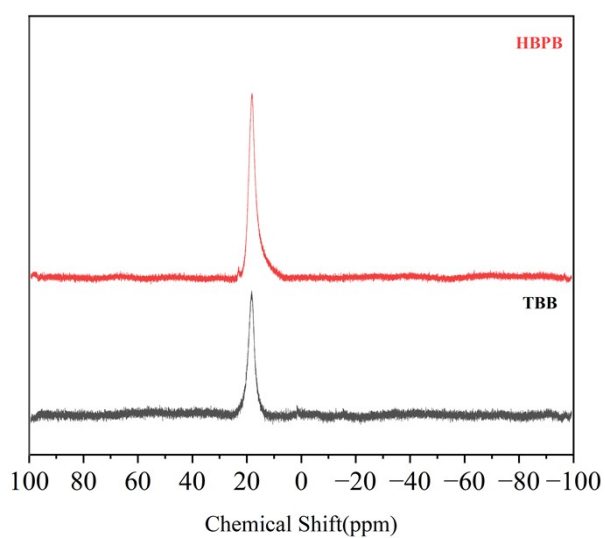
The difference in the volume of NaOH standard titration solution consumed between the blank tests and the sample should be between 10 mL and 15 mL. If the difference in volume is greater than 15 mL, it indicates that the sample mass is too large and should be reduced. Conversely, if the difference in volume is less than 10 mL, it indicates that the sample mass is too small and should be increased.

Table S2 Titrimetric results of -OH content in HBPB

Test number	c (mol·L ⁻¹)	V_0 (ml)	V_1 (ml)	m (g)	$I_{(OH)}$ (mmol·g ⁻¹)
Controlled 1	0.5	87.60	—	—	
Controlled 2	0.5	87.40	—	—	
Controlled 3	0.5	87.70	—	—	
Average	0.5	87.57	—	—	
1	0.5	87.57	72.70	0.4914	15.15×10^{-3}
2	0.5	87.57	73.40	0.4368	15.19×10^{-3}
3	0.5	87.57	74.30	0.4373	15.17×10^{-3}
Average	—	—	—	—	15.17×10^{-3}

S 2.3 The ¹¹B NMR spectra of TBB and HBPB.

The ¹¹B NMR spectra of TBB and HBPB exhibit similar chemical shifts at 18.52 ppm, further confirming the successful synthesis of HBPB.

Figure S2 ¹¹B NMR spectra of TBB and HBPB.

Supplementary information S3

S 3.1 Quality change rate of materials through solvent resistance experiment

$$\text{Mass change rate} = \frac{W_1 - W_0}{W_0} \quad (2)$$

Table S3 Results of sample mass change and mass change rate

Solvent	Immersion time(days)	Sample	W_0 (g)	W_1 (g)	Mass change rate (%)
ethanol	1	HTPB-0	3.1584	3.1611	0.0855
		HTPB-2	3.5813	3.5825	0.0335
	4	HTPB-0	3.2862	3.2909	0.1430
		HTPB-2	3.1789	3.1824	0.1101
	7	HTPB-0	3.4472	3.4571	0.2872
		HTPB-2	3.4904	3.4985	0.2321
methanol	1	HTPB-0	3.4586	3.4650	0.1850
		HTPB-2	3.4745	3.4789	0.1266
	4	HTPB-0	3.2569	3.2660	0.2794
		HTPB-2	3.6311	3.6387	0.2093
	7	HTPB-0	3.2794	3.2982	0.5733
		HTPB-2	3.1524	3.1633	0.3458
acetone	1	HTPB-0	3.3371	3.3484	0.3386
		HTPB-2	3.3570	3.3652	0.2443
	4	HTPB-0	3.5549	3.5821	0.7651
		HTPB-2	3.2932	3.3126	0.5891
	7	HTPB-0	3.2328	3.2769	1.3641
		HTPB-2	3.4769	3.5075	0.8801
dichloromethane	1	HTPB-0	3.2783	3.2179	-1.8424
		HTPB-2	3.3147	3.2753	-1.1886
	4	HTPB-0	3.4410	3.3556	-2.4818
		HTPB-2	3.1020	3.0409	-1.9697
	7	HTPB-0	3.3345	3.2200	-3.4338
		HTPB-2	3.4317	3.3493	-2.4011

To evaluate the solvent resistance of the materials, both unmodified HTPB and HBPB-modified HTPB samples were subjected to immersion tests in various organic solvents. The samples were immersed in ethanol, methanol, acetone, and dichloromethane for different durations: one day, four days, and seven days. The initial weight of each sample (W_0) was accurately measured before immersion. After the specified immersion periods, the samples were removed from the solvents, quickly rinsed with distilled water to remove any residual solvent, and gently wiped dry. The samples were then placed in an oven and dried to a constant weight. The final weight of each sample (W_1) was recorded. The mass change rate for each sample was calculated using Equation (2).

Based on the results in Table S3, both HTPB-0 and HTPB-2 exhibited certain mass changes after being immersed in the four solvents. The mass of the samples in ethanol, methanol, and acetone increased gradually with the immersion time, while in dichloromethane, the mass decreased over time. The mass change rate in ethanol, methanol, and acetone followed the overall trend of acetone > methanol > ethanol. This is because ethanol molecules have relatively weak polarity and lower penetration ability, whereas methanol molecules are smaller and have stronger polarity compared to ethanol, resulting in a higher mass change rate. Acetone, with its strong penetration ability, caused significant mass increase due to the absorption of a large amount of solvent molecules. Dichloromethane, on the other hand, has a strong dissolving effect, which may lead to partial degradation or dissolution of the polymer, thus reducing the mass of the material. HBPB-modified HTPB, with its higher crosslinking density and enhanced intermolecular interactions, exhibited lower mass change rates in all four solvents compared to pure HTPB.