Support Information

Smart Boron Nitride Nanosheets Embedded Adhesives with switchable adhesion and oxidation resistance

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Supporting information includes experimental details for preparation and characterization of BNNSs, DMA, MPEG and hybrid adhesives, detailed procedure of lap shear tests, detailed procedure of anti-bacterial experiments, detail calculation of work of adhesion, detailed calculation of dielectric parameters (PDF) and five videos as following.
The facture process of glass in lap shear test (AVI, Video S1)
Formation of P(DMA-r-DMAEMA-r-MPEG)@ BNNS-NH_2 gel (AVI, Video S2)
Debonding of P(DMA-r-DMAEMA-r-MPEG)@ BNNS-NH_2 gel (AVI, Video S3)
Reforming of P(DMA-r-DMAEMA-r-MPEG)@ BNNS-NH_2 gel (AVI, Video S4)
Selective pH-induced releasing of PDMS from glass (AVI, Video S5)

1 Materials

4-formylbenzoic acid, N-(3-dimethylamino propyl)-N’-ethylcarbodiimide hydrochloride (EDC·HCl), dopamine hydrochloride, methacryloyl chloride, 2-(Dimethylamino)ethyl methacrylate and *h*-BN powder were purchased from Aladdin. 4-(Dimethylamino) pyridine (DMAP), Poly(ethylene glycol) methacrylate (MPEG, average Mn = 360 g/mol) and di-*tert*-butylperoxide were obtained from Sigma-Aldrich. γ-aminopropyltriethoxysilane (KH550, 98 %), azodiisobutyronitrile (AIBN), sodium tetraborate decahydrate, sodium bicarbonate, hexane, 1, 4-dioxane, dichloromethane (DCM), tetrahydrofuran (THF), ethyl acetate, concentrated sulfuric acid and hydrogen peroxide were purchased from Sinopharm Chemical Reagent.

2 Synthesis of N-(3, 4-dihydroxyphenethyl) methacrylamide (DMA)

DMA was synthesized following previous reported methods with some modifications.[1] Briefly, sodium tetraborate decahydrate (20 g) and sodium bicarbonate (8 g) were dissolved in deionized water (200 mL) and bubbled with argon (Ar) for 20 min, followed by the addition of dopamine-HCl (10 g). Next, methacryloyl chloride (8.6 mL) in THF (50 mL) and 1 M NaOH solution were simultaneously added dropwise using syringe pump under Ar atmosphere within 2 h. The pH of the mixture solution was monitored by pH-meter and maintained above 8. After 14 h of reaction at 25 °C under Ar bubbling, the modena slurry was filtrated and washed with ethyl acetate (100 mL). The synthesized clear modena solution was acidified with 1 M HCl to pH less than 2 and turned to pale yellow, followed by extraction with ethyl acetate (100 mL) for three times. The resultant brown extract was dried over anhydrous MgSO4 and rotary evaporated to around 50 mL of volume. After being precipitated into 500 mL hexane and stored at 4 °C overnight, the brown product was dried in a vacuum oven and detected by ^{1}HNMR (Figure S1a).

^{1}H NMR (400 MHz, DMSO) δ 8.76 (s, 1H), 8.64 (s, 1H), 7.94 (t, J = 5.5 Hz, 1H), 6.63 (d, J = 7.9 Hz, 1H), 6.58 (d, J = 2.0 Hz, 1H), 6.43 (dd, J = 8.0, 2.0 Hz, 1H), 5.62 (s, 1H), 5.31 (dd, J = 8.2, 6.7 Hz, 1H), 3.28 – 3.10 (m, 2H), 2.55 (dd, J = 15.4, 8.1 Hz, 2H), 1.84 (s, 3H).

3 Synthesis of aldehyde group functionalized MPEG

Poly(ethylene glycol) methacrylate (MPEG360, 3.6000g, 10mmol), 4-formylbenzoic acid (1.8016g, 12mmol) and N-(3-dimethylamino propyl)-N'-ethylcarbodiimide hydrochloride (EDC·HCl, 2.8755g, 15mmol) were dissolved in the mixture of THF and DCM (200 mL, 1:1 v/v). 4-(Dimethylamino) pyridine (DMAP, 0.1833g, 1.5mmol) dissolved in 10mL DCM was added dropwise under argon atmosphere. After 16 h of reaction at 25 °C, the solution was washed with aqueous NaOH (1 M), HCl (1 M), saturated $NaHCO_3$ solution and brine sequentially. The organic phase was dried over anhydrous $MgSO_4$ and concentrated to obtain buff viscous liquid product. The prepared functionalized monomer was denoted as FMPEG and determined by ^{1}HNMR (Figure S1b).

^{1}H NMR (400 MHz, DMSO) δ 10.27 – 10.01 (m, 1H), 8.24 – 8.11 (m, 2H), 8.10 – 7.98 (m, 2H), 6.01 (d, J = 17.8 Hz, 1H), 5.77 – 5.55 (m, 1H), 4.53 – 3.42 (m, 28H), 3.35 (s, 3H), 2.51 (dt, J = 3.5, 1.7 Hz, 1H), 1.92 – 1.71 (m, 3H).

4 Synthesis of copolymer P(DMA-r-DMAEMA-r-FMPEG)

The copolymer P(DMA-r-DMAEMA-r-FMPEG) was prepared by solvent polymerization. A typical copolymerization process is described as follows. DMAEMA (2 g, 12.7 mmol), DMA (0.3515g, 1.6

mmol) and FMPEG (1.0052 g, 1.6 mmol) are dissolved in the mixture of 13 mL ethanol and 20 mL 2, 4-dioxane with nitrogen protection. Then AIBN (0.0522g, 0.3 mmol) as an initiator is added into the reactor at 65 °C. After 12 h of polymerization, the crude reaction solution was purified by rotary evaporation to remove most of the solvent. Then, the copolymer was precipitated in diethyl ether for three times, and finally dried in a vacuum oven at 50 °C. The synthesized functionalized copolymers were designated as DDF.

5 Synthesis of amino functionalized boron nitride nanosheets (BNNS-NH_2)

Firstly, *h*-BN were ultrasonically exfoliated in DMF solutions for 48 h (100 W) to decrease the thickness. The supernatant was collected by centrifuging at 3000 rpm for 15 min. BNNSs were obtained by centrifuging the supernatant at 8000 rpm for 15 min and dried at 70 °C. BNNS-NH_2 was then prepared by a three-step synthesis according to previous reported methods with some modifications.[2] Briefly, (1) exfoliated BNNSs (65 mg) in di-*tert*-butylperoxide (130 mL) was dispersed by sonication for 6 h and then sealed in a teflon-lined stainless-steel autoclave. The autoclave was heated to 120 °C and rotational blended at 50 rpm by homogeneous reactor for 12 h. After cooling to room temperature, the white product was filtered and washed with chloroform and ethanol, followed by vacuum dried at 50 °C for 12 h. (2) *tert*-butoxy functionalized BNNSs (50 mg) in concentrated sulfuric acid (75 mL) was sonicated for 1 h and sequently added with freshly opened hydrogen peroxide (25 mL) dropwise. The mixture was vigorously stirred for 5 h at room temperature and then diluted with deionized water. After filtering and washing to neutral, the hydroxyl functionalized BNNSs (BNNS-OH) product were collected and dried in vacuum for 12 h at 50 °C. (3) BNNS-OH (100 mg) in the mixture of water and ethanol (200 mL, 13:187 by volume) was sonicated for 30 min. After that, KH550 (29 mg) was introduced to the slurry dropwise and refluxed for 12 h at 70 °C. The final product amino modified BNNSs (BNNS-NH_2) were washed three times with ethanol and dried in vacuum at 50 °C for 4 h. The modified amount of amino was characterized by EDS. TGA and DSC were conducted to analysis thermal data of BNNS-NH_2 powder (TGA/DSC3+, Mettler Toledo). The sample was heated at 10 °C/min in air atmosphere from 50 to 100°C and stabilized at 100 °C for 20 min to remove the moisture, then reheated from 100 to 900°C. The mass and heat flow profiles with increasing temperature were recorded. The weight percent of modified KH550 in BNNS-NH_2 powder was determined to be 5.71% and the decomposition temperature of it was around 273.3 °C (Figure S12).

6 Surface work of adhesion (W_{SA})[3]

Surface work of adhesion is used to evaluate the strength of interfacial interaction and can be calculated by the following equation (Equation 1).

$$W_{SA} = 2\sqrt{\gamma_1^d \gamma_2^d} + 2\sqrt{\gamma_1^p \gamma_2^p} \quad (1)$$

Here, γ^d and γ^p represent dispersion and polar interactions of the dried solid surfaces, which can be obtained by measuring the contact angles (θ) of at least two assigned liquids on the solid surface and counted by the Young equation (Equation 2) as following.

$$\gamma_l(1 + \cos\theta) = 2\sqrt{\gamma_l^d \gamma_s^d} + 2\sqrt{\gamma_l^p \gamma_s^p} \quad (2)$$

$$\gamma_l = \gamma_l^d + \gamma_l^p \quad (3)$$

Here, we chose water ($\gamma_{water}^d = 21.8\,mN/m,\ \gamma_{water}^p = 51.0\,mN/m$) and *n*-Hexadecane ($\gamma_{hexa}^d = 26.3\,mN/m,\ \gamma_{hexa}^p = 0\,mN/m$) as probe liquids. Different polymer mixtures (0.5 g/mL, ethanol) were sprayed onto glass slides by a spray gun (nozzle diameter, 0.5 mm; HD® 180, NO 302, Taiwan) at a spraying pressure of 1 bar and distance of 10 cm, followed by drying in vacuum overnight.

7 Lap shear adhesion test

Bonding strength are measured by lap shear test according to ASTM D1002 lap shear test guideline. First, copolymer P(DMA-r-DMAEMA-r-FMPEG) solution (100 µL, 0.5 g/mL) in ethanol: water (1:1, v/v) was deposited onto the surface of certain substrate (glass, aluminum, stain steel, PS and PTFE) using pipette. Next, another substrate was placed on it and the overlap area is about 25×15 mm. Before test, 20 g weight were placed on the joint places 10 min for stabilization followed by 12 h room temperature stewing process. Different substrates are applied with corresponding fixture, for example, brittle glasses were immobilized with alloy gripper carrying elastic rubber inside while another substrates were fixed by screws (Figure S2). To perform this experiment, two substrates glued together were pulled in opposite directions that parallel to the bonding plane. Tensile shear strength (MPa) equal to the maximum tensile force (N) divided by the overlap area (mm^2) joined by adhesives.

8 Mechanical property tests of NCAs.

For mechanical tests, different polymer mixtures were poured into silicone molds and then dried in vacuum oven under room temperature to give uniform rectangular samples without remaining solvents or any bubbles. The obtained samples were cut into a few dumbbell shaped specimens (GB/T-528 IV). Five film samples with different BNNS-NH$_2$ charging rate were prepared according to the recipe listed in Table 3.

9 Dielectric properties of NCAs

Samples were cut into square shape with short length of about 15mm and thickness of about 1 mm. Dielectric loss and capacitance (C) were recorded by Aglient LCR meter (E4980A) with the operating frequency ranging from 20 to 2×10^6 Hz at room temperature. Dielectric constant (ε) was calculated by the equation (Equation 4) as following.

$$\mathrm{C} = \frac{\varepsilon \mathrm{S}}{4\pi k d} \quad (4)$$

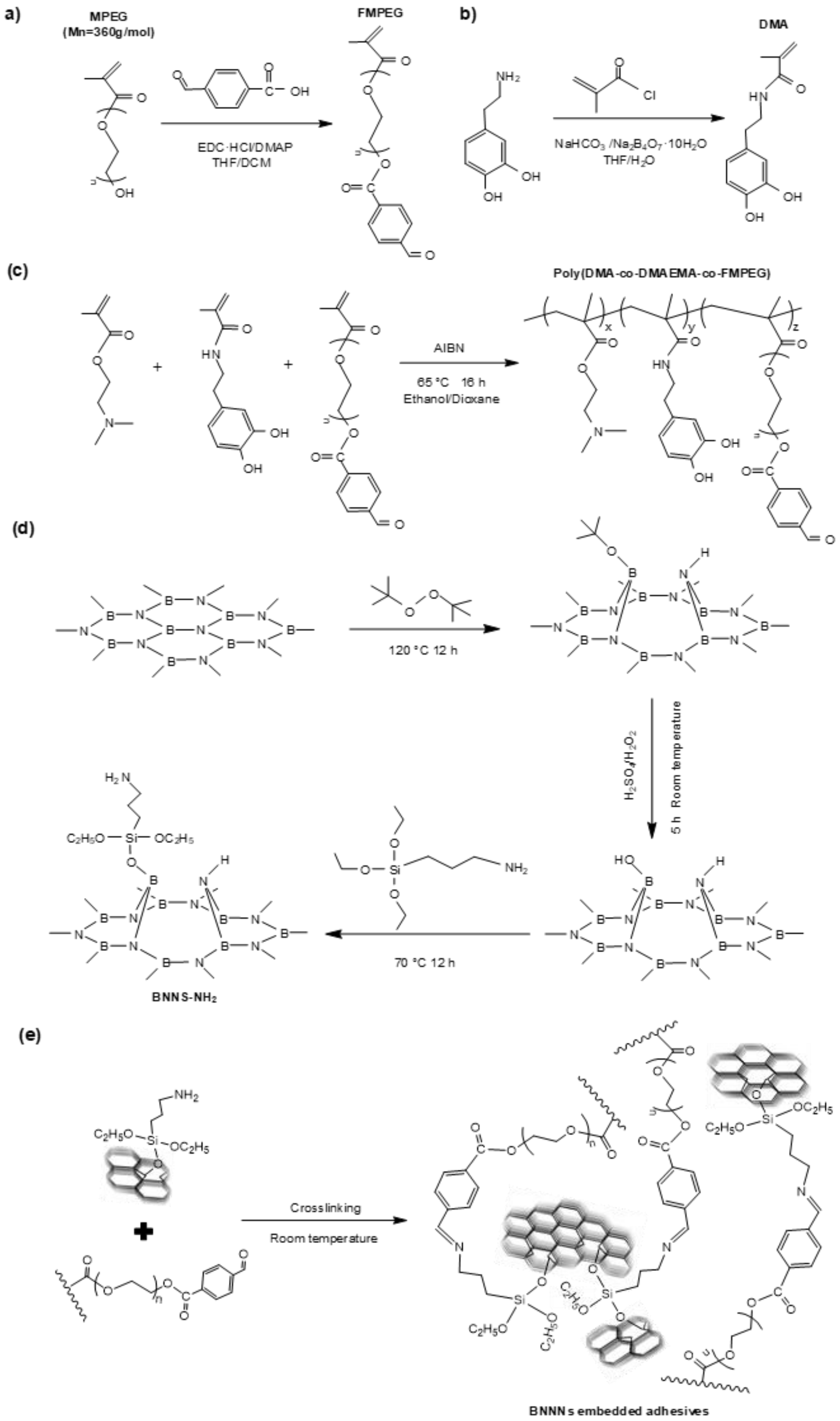
Here, S is the overlap area of a capacitor pair which is 1.1310 cm^2. k, electrostatic constant, equal to 9.0×10^6 $\mathrm{N{\cdot}m}^2$. d is the thickness of prepared samples.

10 Antibacterial performance of NCAs[4]

Plate count method was applied to investigate the effect of resultant adhesives against *C. glutamicum* and *E. coli.* A cluster of *C. glutamicum* and *E. coli* taken from original LB solid medium were incubated in test tube with 5 mL LB liquid medium overnight followed by being transferred into conical flask with 50 mL LB liquid medium until reaching the exponential growth period. Coverslips (2.2×2.2 cm^2) coated with different amount of BNNSs doped adhesives were immersed and incubated in 5 mL above E. coli suspension or C. glutamicum suspension at 37 °C and 30 °C for 3 h, respectively. The coverslips were then gently washed with 10 mL PBS buffer to collect the adherent bacteria followed by diluting to five 10-fold thinners. 100 μL of the decimal dilutions were spread on the petri dishes filled with LB agar and then incubated at 37 °C and 30 °C separately until the colonies became clear and distinct. Surviving bacteria were counted represented by the amount of colonies and the bactericidal rate (E) was calculated as following (Equation 5):

$$\mathrm{E} = \frac{A-B}{A} \times 100\% \qquad (5)$$

Here, A and B is the number of the colonies corresponding to blank and adhesives processed coverslips.



Scheme S1 Synthetic route for preparing NCA

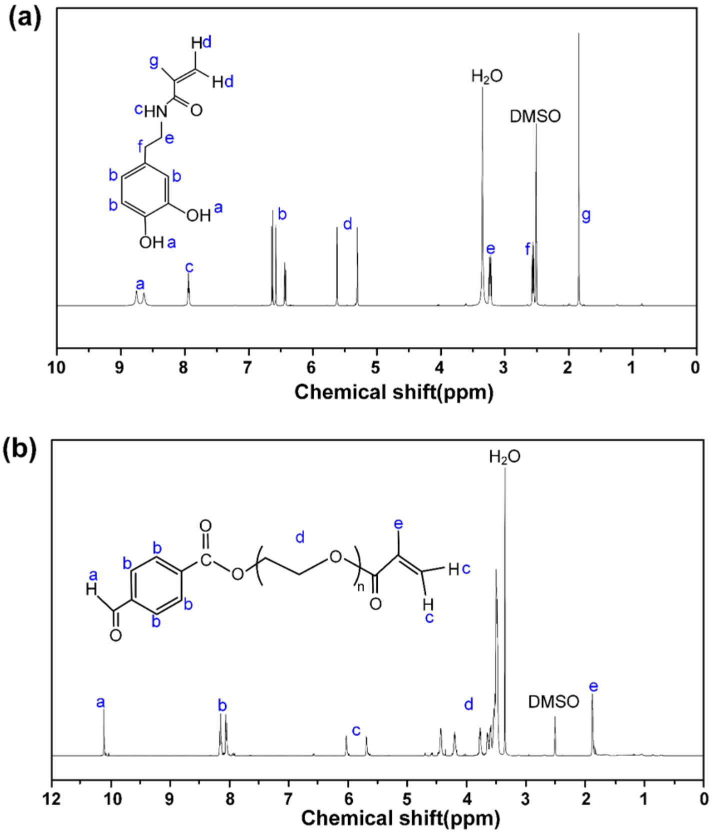
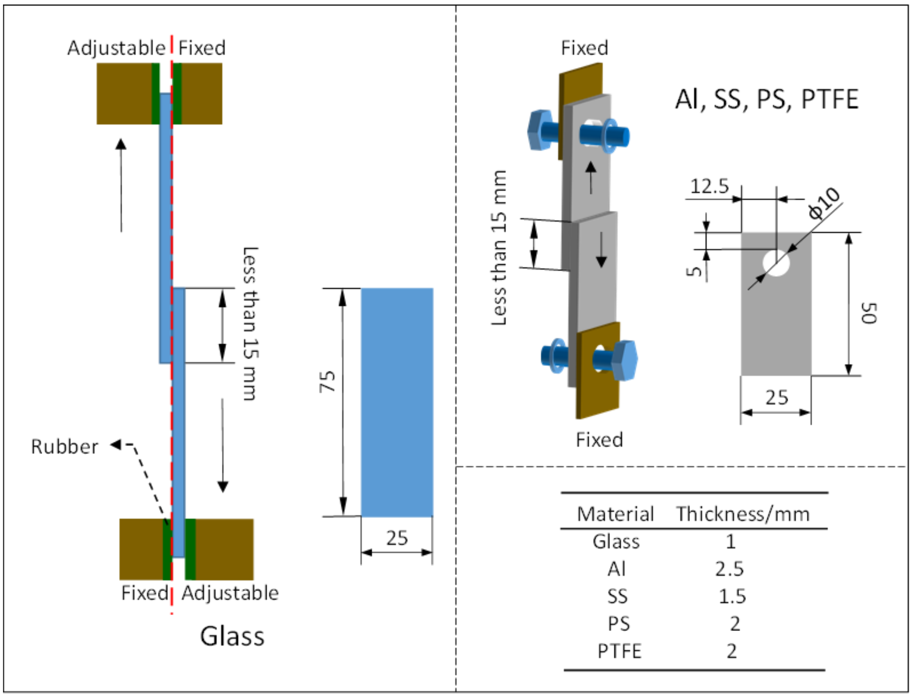


Figure S1 ^{1}HNMR spectra of DMA and FMPEG



Material	Thickness/mm
Glass	1
Al	2.5
SS	1.5
PS	2
PTFE	2

Figure S2 Illustration of lap shear test molds (units: mm)

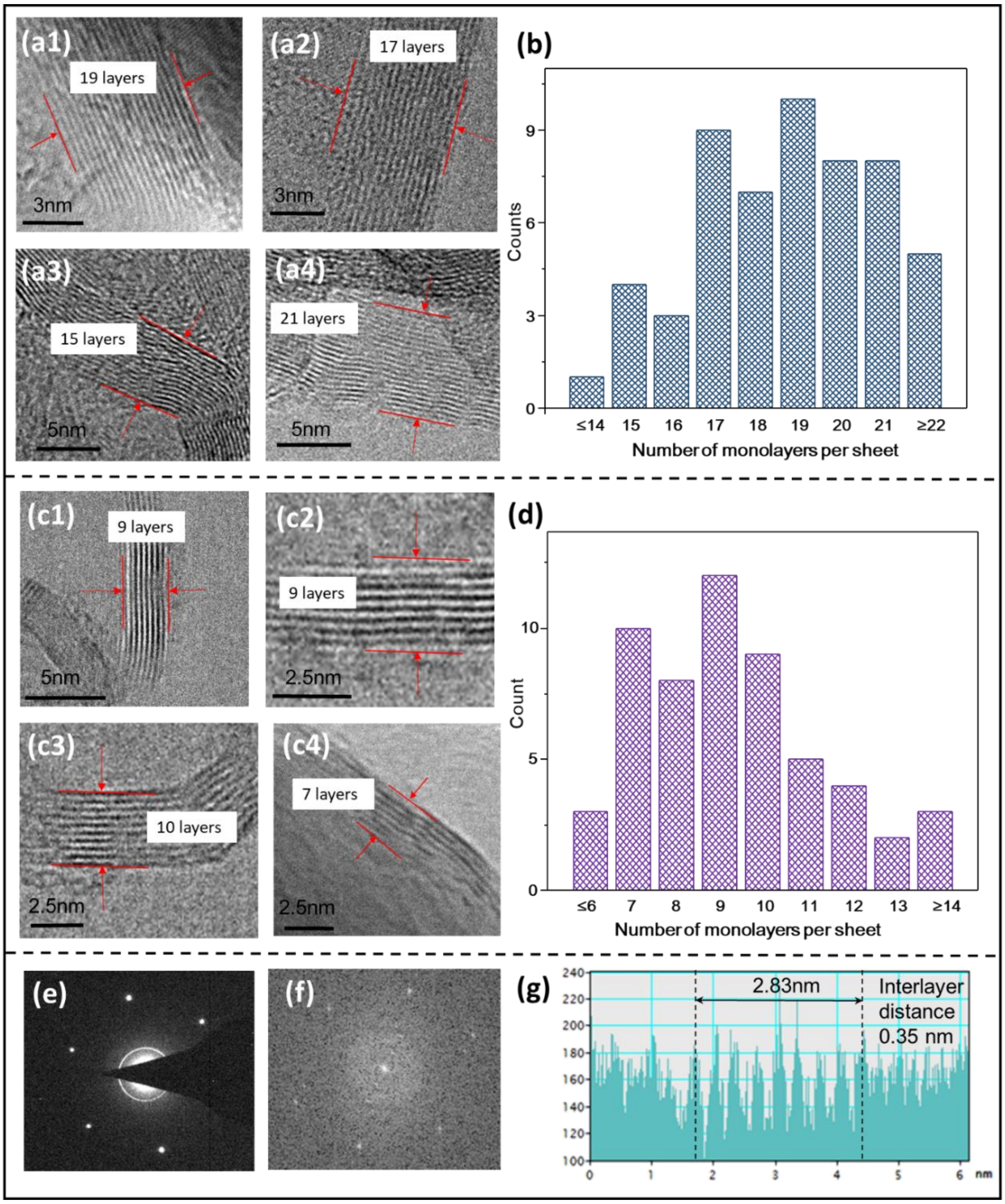
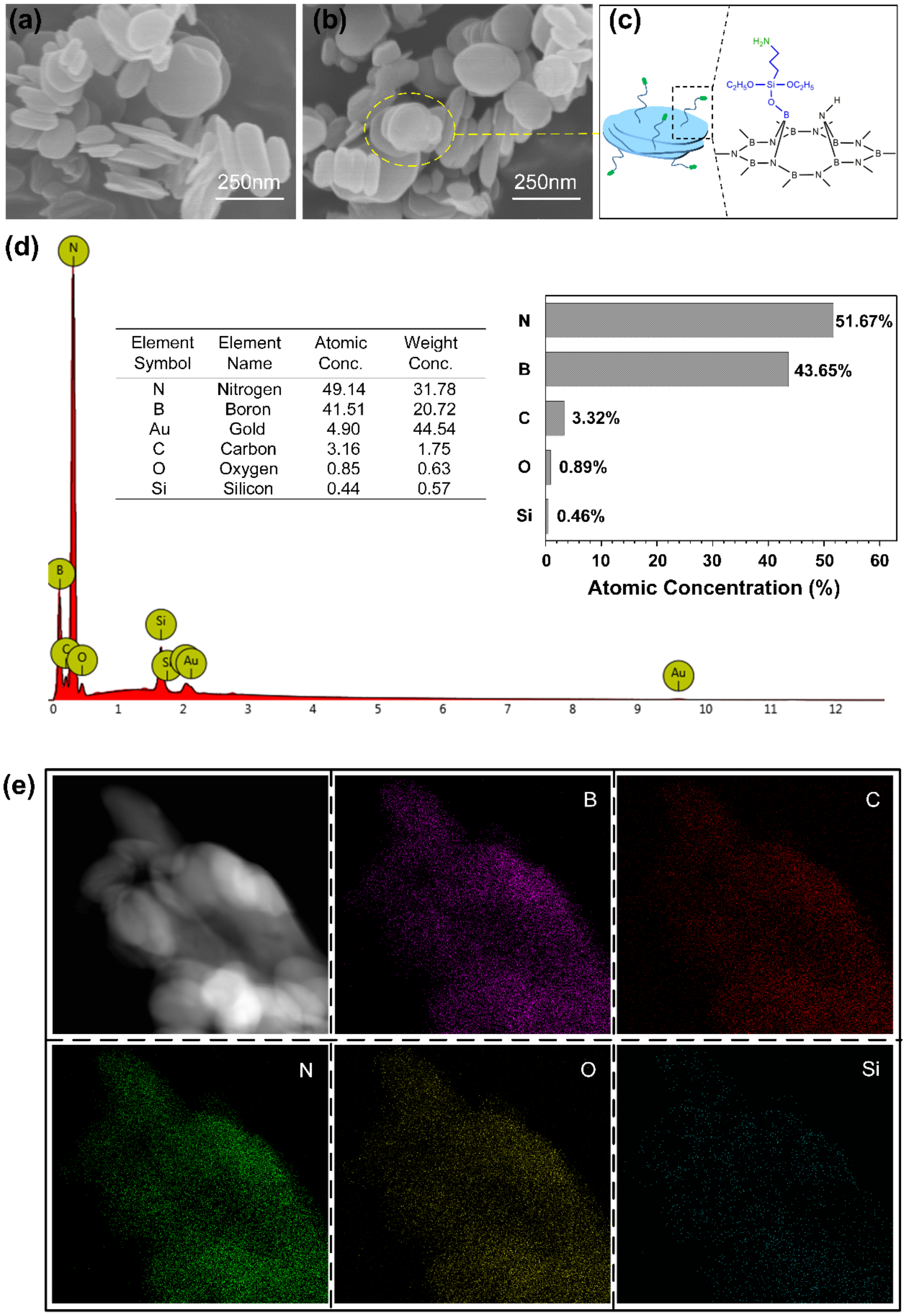


Figure S3 (a) TEM and (b) boron nitride nanosheet numbers of original BNNSs (55 pieces); (c) TEM and (d) boron nitride nanosheet numbers of exfoliated BNNSs (55 pieces); (e) Electro-diffraction diagram of exfoliated BNNSs; (f) Corresponding fast Fouier transform of exfoliated BNNSs; (g) Interlayer distance calculation by DigitalMicrograph.

After ultrasonic exfoliating process, the thickness distribution of BNNSs apparently shifted to a lower value range. Figure S3e and S3f confirmed the hexagonal symmetric crystalline structure of BNNS has not been damaged. Interlayer distance calculated by DigitalMicrograph is 0.35 nm, which is the same as theoretical value.



Element Symbol	Element Name	Atomic Conc.	Weight Conc.
N	Nitrogen	49.14	31.78
B	Boron	41.51	20.72
Au	Gold	4.90	44.54
C	Carbon	3.16	1.75
O	Oxygen	0.85	0.63
Si	Silicon	0.44	0.57

Figure S4 SEM of BNNS (a) before being exfoliated and (b) after being exfoliated and decorated with amino groups; (c) Chemical structure of amino modified BNNS; (d) EDS spectrum of BNNS-NH_2; (e) Element mapping of BNNS-NH_2 established using EDS.

Figure S4a and S4b demonstrated the sheet structure of *h*-BN was not been influenced by the ultrasonic and following chemical modification process. Based on EDS results of BNNS-NH_2 monolayer (Figure S4d), the graft density was calculated to be about 0.2 grafted amino groups per nm^2 of BNNS area (calculate as following). The grafted amino groups evenly distributed on the BNNSs according the Si element mapping of BNNS-NH_2 (Figure S4e).

According to the reference[2] and as shown in Scheme S1, the chemical structure of KH550 displays that the modified amino number equals to the silicon number. The atomic concentrations of Si and B is 0.46% and 43.65% (Figure S4d). The graft density x_{amino} of amino number can be calculate by the following equation:

$$x_{amino} = \frac{Atom(Si)}{Atom(B)} = \frac{0.46\%}{43.65\%} = 0.01054$$

This value represents every B-N hexagonal ring grafts 0.01054 averagely.

For more clearly, we calculate the graft density per area. Taking the BN nanosheets with the diameter of about 200 nm as example in yellow circle in Figure S4b. We consider the area of it $S_{200\,nm}$ equals to circle area approximatively and can be calculate by the following equation:

$$S_{200\,nm} = \left(\frac{D}{2}\right)^2 \pi = \left(\frac{200}{2}\right)^2 \pi = 3.14 \times 10^4 \ \text{nm}^2$$

The distance of the near two hexagonal ring is 0.25 nm.[2] Therefore, the area of every single hexagonal ring $S_{single\ hexagonal\ ring}$ can be calculate by the following equation:

$$S_{single\ hexagonal\ ring} = \frac{0.25}{\sqrt{3}} \times \frac{0.25}{2} \times \frac{1}{2} \times 6 = 5.413 \times 10^{-2} \ \text{nm}^2$$

Thus, the number of single hexagonal rings $n_{single\ hexagonal\ ring}$ in the BN nanosheet with the diameter of about 200 nm is:

$$n_{single\ hexagonal\ ring} = \frac{S_{200\,nm}}{S_{single\ hexagonal\ ring}} = \frac{3.14 \times 10^4}{5.413 \times 10^{-2}} = 5.8 \times 10^5$$

The amino number $n_{amino\ number}$ of BN nanosheet with diameter of 200 nm is:

$$n_{amino\ number} = x_{amino} n_{single\ hexagonal\ ring} = 6.113 \times 10^3$$

Therefore, the amino number per area is:

$$x_{amino\ per\ area} = \frac{n_{single\ hexagonal\ ring}}{S_{200\,nm}} = \frac{6.113\times10^3}{3.14\times10^4} = 0.2 \ \text{nm}^{-2}$$

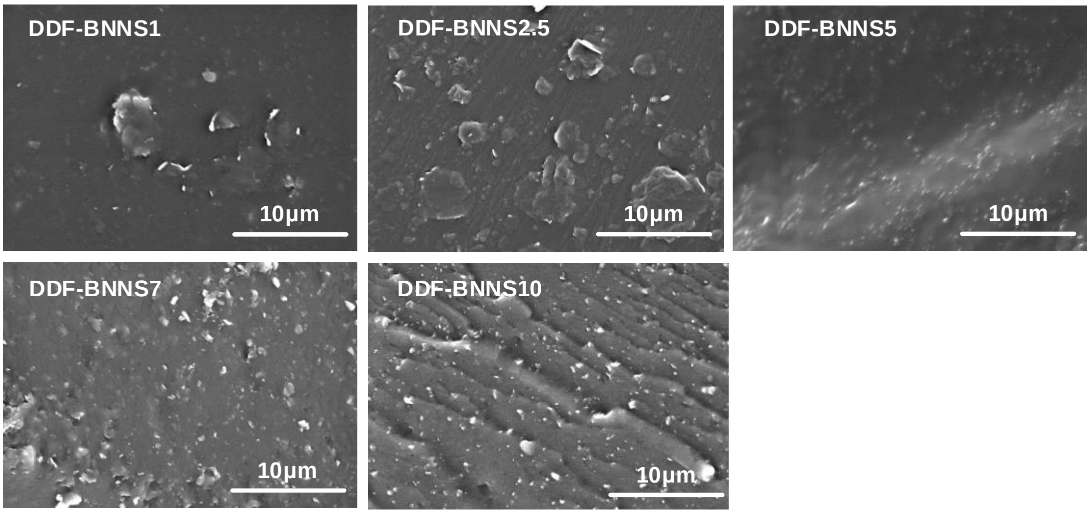


Figure S5 Cross section SEM images of DDF-BNNSs

Cross-sectional SEM images of DDF-BNNSs also reveals that amino-functionalized BNNSs are evenly distributed in copolymer without apparent agglomeration with the increasing addition.

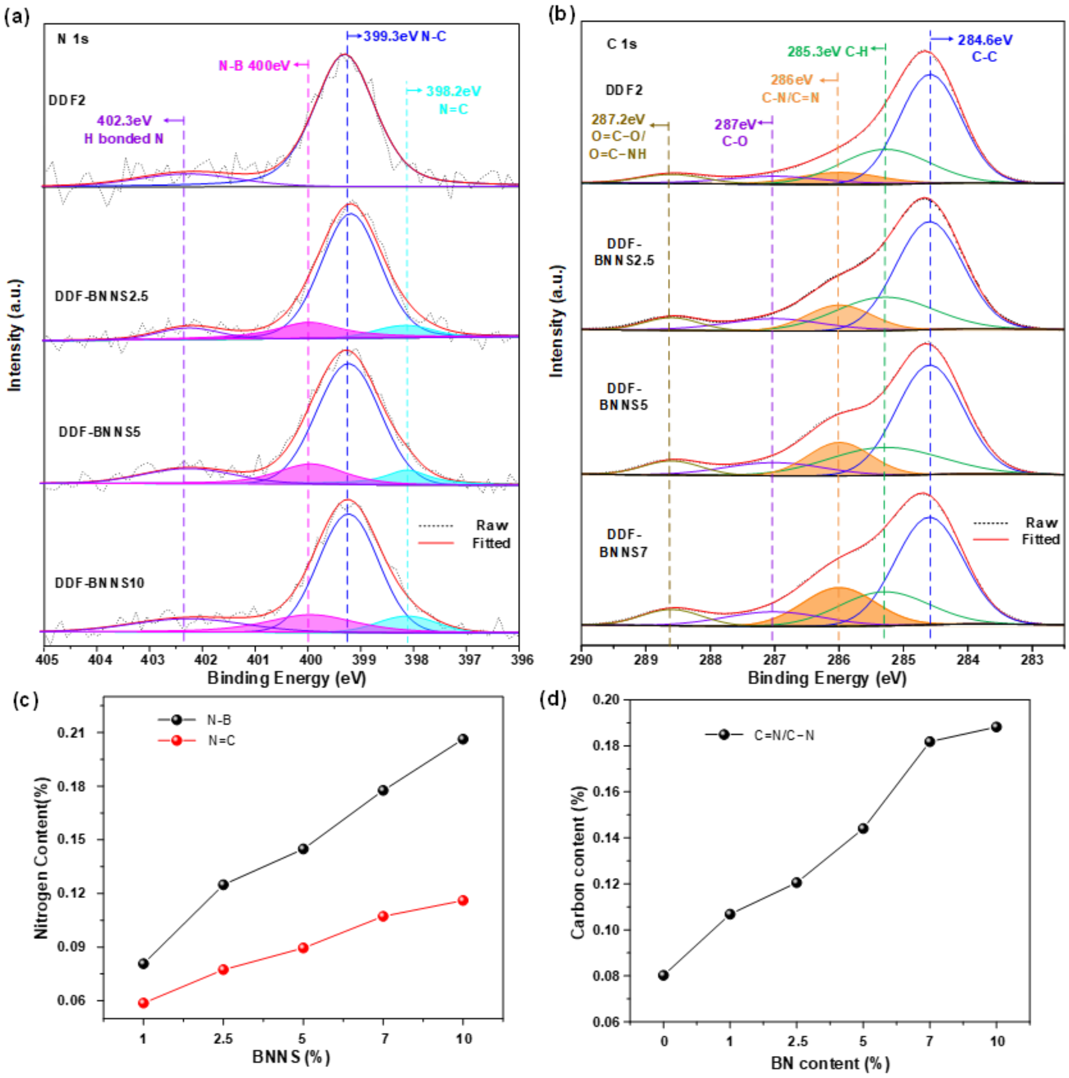


Figure S6 (a) N 1s core-level and (b) C 1s core-level spectra of DDF2, DDF-BNNS2.5, DDF-BNNS5 and DDF-BNNS7. (c) N−B and N=C concentration as a function of BNNS-NH_2 addition (d) C=N/C−N concentration at various BNNS-NH_2 contents.

N 1s and C 1s core-level spectra of DDF2, DDF-BNNS2.5, DDF-BNNS5 and DDF-BNNS7 shows that the intensity of N=C, N−B, and C=N/C−N species increase significantly with increasing content of BNNS because the formation of crosslinked Schiff base network.

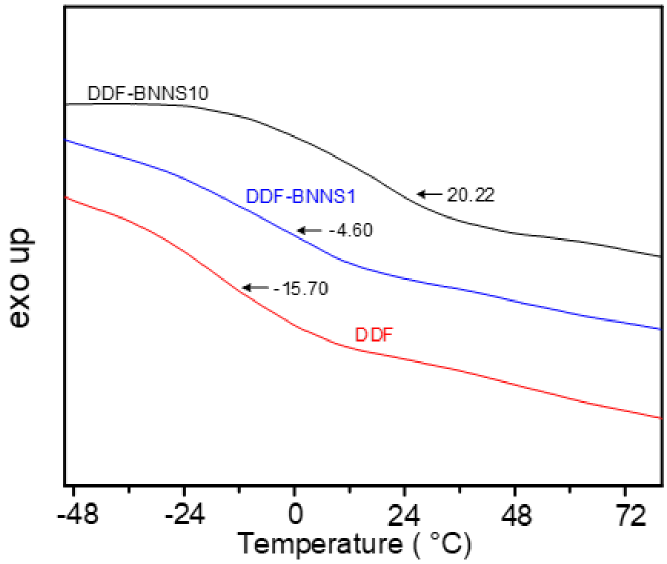


Figure S7 DSC thernograms of DDF, DDF-BNNS1 and DDF-BNNS10. The heating rate is 10 °C/min.

Figure S8 Adhesion performance of DDF-BNNS2.5 for glass

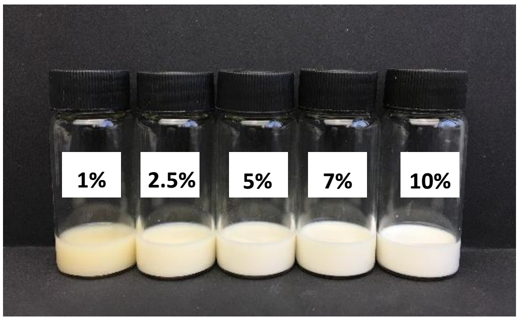


Figure S9 Samples to be sprayed on glasses for contact angle measurements.

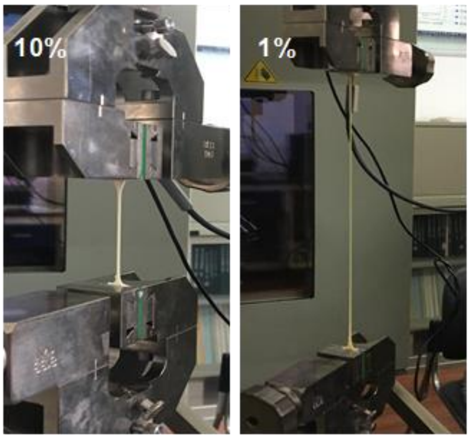


Figure S10 Photos illustrating the stretching of DDF-BNNS10 (left) and DDF-BNNS1 (right) recorded in mechanical property tests.

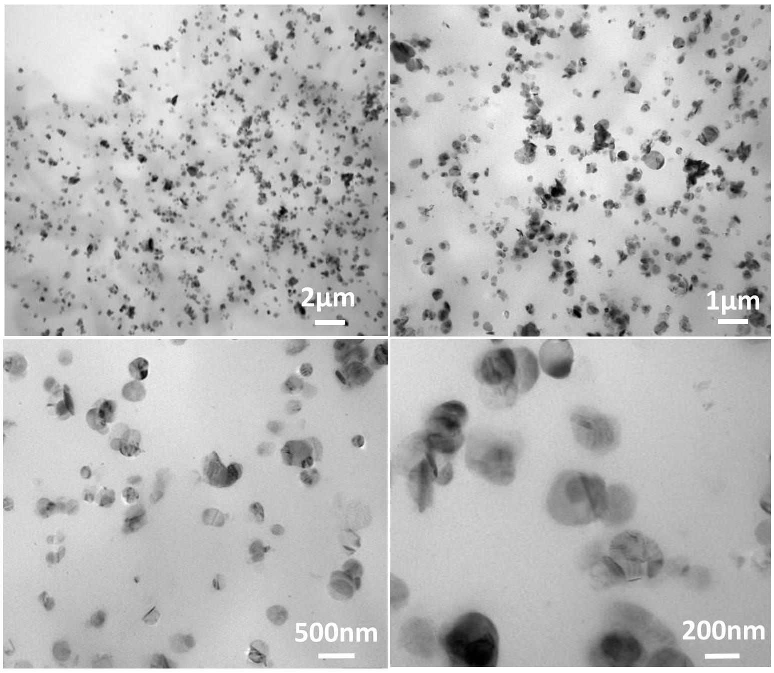


Figure S11 TEM images of DDF-BNNS10 with different magnification, 5000×, 10000×, 20000×, 50000×.

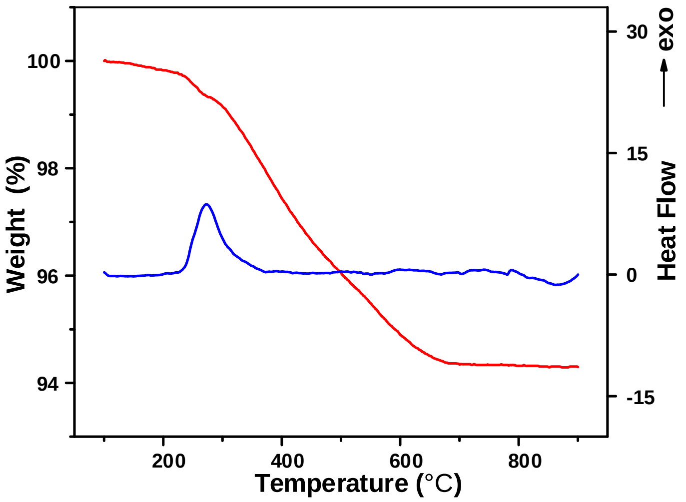
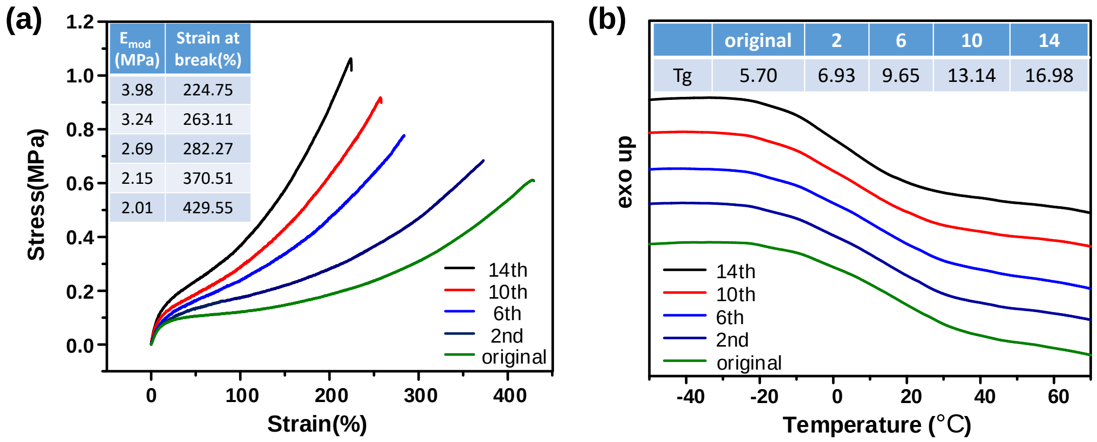


Figure S12 TGA and DSC curves of BNNS-NH$_2$



E_{mod} (MPa)	Strain at break(%)
3.98	224.75
3.24	263.11
2.69	282.27
2.15	370.51
2.01	429.55

	original	2	6	10	14
Tg	5.70	6.93	9.65	13.14	16.98

Figure S13 TGA and DSC curves of DDF-BNNS5 after different cycles

Table S1 N concentrations of various samples

Sample	H bonded N 402.3ev	N−B 400ev	N−C 399.3ev	N=C 398.2ev
DDF	13.18%	/	86.82%	/
DDF-BNNS1	8.92%	8.07%	77.14%	5.87%
DDF-BNNS2.5	6.72%	12.49%	73.05%	7.74%
DDF-BNNS5	9.75%	14.49%	66.81%	8.95%
DDF-BNNS7	8.99%	17.76%	62.53%	10.72%
DDF-BNNS10	8.58%	20.63%	59.18%	11.61%

Table S2 C concentrations of various samples

Sample	C–C 284.6ev	C–H 285.3 ev	C=N/C–N 286 ev	C–O 287 ev	O=C–O/ O=C–NH 288.6 ev
DDF2	54.94%	24.92%	8.02%	7.21%	4.87%
DDF-BNNS1	51.08%	25.55%	10.68%	7.70%	4.98%
DDF-BNNS2.5	50.86%	23.00%	12.05%	9.18%	4.90%
DDF-BNNS5	49.75%	21.36%	14.40%	8.93%	5.56%
DDF-BNNS7	46.88%	19.47%	18.18%	9.22%	6.24%
DDF-BNNS10	47.66%	19.04%	18.82%	8.61%	5.87%

Table S3 Surface work of adhesion for various samples

Sample	WCA[a] (^{o})	HCA[b] (^{o})	γ_s^d (mN/m)	γ_s^p (mN/m)	γ_s (mN/m)	W_{SA} (mJ/m^2)
Glass	22.99	24.06	24.06	43.32	67.39	/
DDF1	77.72	25.74	23.76	8.97	32.73	87.24
DDF2	73.39	24.08	24.06	11.21	35.27	92.19
DDF3	74.66	20.01	24.74	10.20	34.94	90.84
DDF-BNNS1	71.72	23.78	24.12	12.15	36.26	94.06
DDF-BNNS2.5	70.70	23.35	24.19	12.72	36.91	95.20
DDF-BNNS5	72.42	23.59	24.15	11.72	35.87	93.28
DDF-BNNS7	75.43	24.16	24.05	10.07	34.12	89.89
DDF-BNNS10	80.38	26.64	23.58	7.70	31.28	84.16

[a] WCA: water contact angle. [b] HCA: n-hexadecane contact angle.

Table S4 Mechanical properties for various samples

Sample	Young's modulus (MPa)	Max tensile strength (MPa)	Fracture energy/ toughness (MJ/m^3)	Strain at break (%)
DDF-BNNS1	0.07	0.02	44.44	2669.08
DDF-BNNS2.5	0.87	0.49	99.61	440.32
DDF-BNNS5	2.01	0.62	117.01	429.55
DDF-BNNS7	3.19	0.77	138.35	375.57
DDF-BNNS10	5.22	1.00	147.09	231.08

Table S5 Bonding strength for various samples

Sample	Glass (MPa)	PS (MPa)	Al (MPa)	SS (MPa)	PTFE (MPa)
DDF1	0.60±0.05	0.91±0.06	0. 43±0.09	0.39±0.10	0.16±0.08
DDF2	0.80±0.06	0.83±0.15	0.53±0.05	0.92±0.12	0.23±0.02
DDF3	0.74±0.13	1.02±0.19	0. 45±0.04	1.09±0.10	0.15±0.04
DDF-BNNS1	/	1.08±0.14	1.92±0.07	2.51±0.04	0.33±0.14
DDF-BNNS2.5	/	1.62±0.08	2.39±0.03	3.15±0.04	0.42±0.17
DDF-BNNS5	/	1.97±0.04	4.18±0.27	3.58±0.04	0.21±0.07
DDF-BNNS7	/	1.44±0.04	5.20±0.11	4.75±0.09	0.21±0.06
DDF-BNNS10	/	1.13±0.06	3.25±0.03	3.83±0.08	0.24±0.05

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Adhesive: A Comparative Study of Catechol and Gallol. *Biomacromolecules* **2017**, 18, 2959-2966.

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