S2.3 Characterization

The morphology of neat TATB and PDA coated TATB was observed with a thin layer of gold before the characterization using a scanning electron microscope (SEM; JSM-6390LV, Zeiss). A detailed topography was also observed using an atomic force microscope (AFM; SPA-300HV, Seiko Instruments) with an SPI 3800 N controller in a tapping mode. Etched silicon tips with a resonance frequency of approximately 70 kHz and a spring constant of about 42 N/m were used for scan. Raman spectra were measured with an FT-Raman spectrometer (DXR Smart Raman). The excitation source was 532 nm from surface plasmon resonance. For each Raman spectrum, the laser beam was focused on the sample at a size of about 2 mm to avoid photochemical decomposition of energetic crystals due to laser exposure, then 10 Raman spectra of 5s each were acquired at 3.0 mW laser power and averaged. The surface chemical composition was measured using X-ray photoelectron spectroscopy (XPS; ThermoFisher spectrometer) equipped with a monochromatic Al K α radiation as an excitation source (hv=1486.6 eV). All measurements were done in hybrid mode, at a 900 take off angle, step size of 0.1 eV, and a spot size of 400 µm. High-resolution scans were acquired for C 1s, N 1s and O 1s regions collected in the fixed analyzer transmission mode. Elemental core-level spectra were fit using Avantage software (ThermoFisher). The binding energy of the spectra was calibrated with respect to C1s peak (C-C, 284.6 eV). After subtraction of a Shirley background, all spectra were fit with the use of a convolution of Lorentzian and Gaussian shapes at a standard ratio of 30:70. The peak-fitting procedure used a minimum number of peaks consistent with the best fit with consideration of peak position, full width at half-maximum, and intensity.

Thermal analysis was performed on a Mettler Toledo instrument by thermogravimetric-differential scanning calorimetry (TG-DSC). The samples were heated from 30 °C to 700 °C at a heating rate of 10 °C/min under nitrogen atmosphere. To evaluate the surface properties, including the dispersive and polar components of the surface energy, which are relevant for evaluating the interfacial interaction between the explosive crystal and polymeric binder, the contact angles of test fluids on the flat surfaces of neat TATB, pTATB pellets and fluoropolymer film were measured statically by a SL200B (Solon Tech. Shanghai Co., Ltd) contact angle instrument. The water, diodomethane and glycerol were selected as test fluids. In addition, a fourth liquid of F₂₃₁₄ solution was also measured in order to give a direct phenomenon of interface affinity between the explosive crystal and F_{2314} binder. Dynamic mechanical analysis (DMA) tests were performed on a dynamic mechanical analyzer of DMA 242C apparatus (Netzsch, Germany) under three point bending mode in the temperature range of 0-150 °C at a frequency of 1 Hz and a heating rate of 1 °C/min, using the samples of $30 \times 10 \times 1.7$ mm³ in size. The three-point bending creep test was conducted using the same DMA apparatus. The mechanical deformation was measured as a function of time under a constant stress level at four temperatures from 30 to 80 °C and three stress levels from 4 to 9 MPa for 5400 s. The Brazilian and compressive tests of the PBX pellets, with dimension of φ 20 mm \times 6

mm and φ 20 mm × 20 mm (diameter × height) respectively, were performed using an Instron 5582 machine (Canton, MA, USA) at the room temperature of 23 °C. The crosshead speed was set at 0.5 mm min⁻¹. At least three specimens of each PBX formulation were tested, and the average values were calculated.

S3 Results and discussion



S3.1 Morphology and characterization

Fig. S1 SEM images for PDA coated TATB for (a) 6 h, (b) 12 h and (c) 24 h.



Fig. S2 Weight percent of PDA coated on TATB as a function of dopamine polymerization time.

sample	R_a / nm	P-V/nm	RMS/nm
(a)	2.12	38.69	3.18
(b)	27.23	403.8	39.72
(c)	39.87	400.0	51.22
(d)	45.21	387.2	57.17
(e)	46.20	358.1	55.95
(f)	50.26	449.9	63.23

Table S1 Parameters from AFM images.

Table S2 XPS atomic concentration of functional groups in all atoms of TATB, PDA, and pTATB.

Atom	Peak positions, eV	TATB	PDA/	pTATB	pTATB	pTATB-
	* '	/%	%	-3h/%	-12h/%	48h/%
C 1s	284.60-284.63(<u>C</u> Hx, <u>C</u> -C)	9.70	36.45	32.25	28.48	30.46
	285.87-286.05(<u>C</u> -OH, <u>C</u> -N)	16.12	26.83	22.81	24.28	24.68
	287.30-288.06(<u>C</u> =O, <u>C</u> -NO ₂)	13.84	5.75	10.96	13.89	12.36
	290.90 (π - π * shake up)		2.18	0.34	1.66	1.80
	Total	39.66	71.21	66.36	68.31	69.30
N 1s	398.45-398.60 (C- <u>N</u> =C)		0.73	0.19	0.31	0.26
	399.40 (Ph- <u>N</u> H ₂)	15.39		3.52	1.82	0.60
	399.98-400.05 (C- <u>N</u> H-C)		7.05	5.21	5.42	6.45
	401.90 (C- <u>N</u> H ₂)		0.67	0.60	0.47	0.80
	405.12-405.25 (Ph- <u>N</u> O ₂)	13.20		2.73	2.70	1.83
	407.84(Ph- <u>N</u> O ₂ Satellitic shake up)	4.56		—	—	
	Total	33.15	8.45	12.25	10.72	9.94
O 1s	531.07-531.24 (C= <u>O</u>)	—	1.14	3.61	2.95	2.79
	532.10-532.16(-NO ₂)	23.95		7.09	6.43	4.12
	533.02-533.08 (C- <u>O</u> H)		19.2	9.62	10.50	13.33
	535.60-535.75(Ph-NO ₂ Satellitic shake up)	3.24	_	1.07	1.09	0.52
	Total	27.19	20.34	21.39	20.97	20.76
N/C		0.836	0.118	0.185	0.157	0.143

Sample	Surface tension (mJ/m ²)			Adhesion work
Samp 1	γ^{d}	γ^{p}	γ	$W_a (mJ/m^2)$
TATB	41.54	3.58	45.12	81.14
pTATB-3h	39.80	5.81	45.61	85.45
pTATB-6h	38.25	7.26	45.51	87.36
pTATB-12h	37.25	9.38	46.63	90.47
pTATB-24h	36.47	10.77	47.24	92.07
pTATB-48h	35.95	11.97	47.92	109.51
F ₂₃₁₄	29.70	17.41	47.11	

Table S3 Surface tension of TATB, pTATB and F2314, as well as interfacial adhesive work between TATB/pTATB and F_{2314} .

S3.3 Thermal properties of TATB and pTATB

The stabilization of energetic materials is essential for practical applications. In this work, the effect of PDA coating on the thermal stability of TATB was evaluated by a TGA-DSC instrument. The obtained curves are displayed in Fig. S3. As shown, all TGA curves showed one-step weight loss. And the PDA coating had nearly no effect on the thermal behavior of TATB. The maximum decomposition temperature of TATB, shown in the DSC curves, had very little change with PDA. Just a little, the decomposition temperature would show a small decrease trend with PDA. From the enlarged profile, we could note that the onset degradation temperature shifted to a lower position for the pTATB which was consistent with the maximum decomposition temperature results, displaying a little decreased thermal stability. As the decomposition temperature of PDA was very close to that of TATB, it was possible that the decomposition products containing amino groups of PDA would have a little promotion effect on the decomposition process of TATB, such as nitro group bond fission, nitro-nitrite isomerization and intramolecular hydrogen transfer.⁶



Fig. S3 Thermal curves of TATB and corresponding PDA coated TATB: (a) TGA;



Fig. S4 Stress dependent creep strain of PBX composites at 60 °C: (a) 7 MPa; (b) 9 MPa.



Fig. S5 Schematic representation of the interfacial interactions of smooth interface and rough interface.