Titanium Diboride-Derived Nanosheets Enhance the Mechanical Properties of Polyurethane: Experiments and Simulation

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Electronic Supplementary Information (ESI)

S1. AFM images of pristine nanosheets (p-NS) and functionalized nanosheets (f-NS) used as fillers for composite preparation.



AFM image of pristine nanosheets (p-NS) and corresponding height profile



AFM image of functionalized nanosheets (f-NS) and corresponding height profile

Figure S1. AFM image of (a) pristine nanosheets (p-NS) and (b) corresponding height profile, (c) functionalized nanosheets (f-NS), and (d) corresponding height profile indicating their thickness in the nano-meter range.

S2. FE-SEM images of neat PU and TiB₂/PU composite films



Figure S2. Microstructural characterization of neat PU and TiB_2/PU composites at 2 wt.% loading. FE-SEM images of (a) neat PU depict feeble spherulitic domains, (b) b- TiB_2/PU , (c) p-NS/PU, and (d) f-NS/PU composite depict prominent spherulitic domains.

As shown in Figure S2, the FE-SEM images of neat PU depict feeble spherulitic domains. In contrast, the FE-SEM images of b-TiB₂/PU, p-NS/PU, and f-NS/PU composites show well-defined spherulitic domains. Moreover, for b-TiB₂/PU and p-NS/PU, the fillers appear deeply embedded within the PU matrix and are not visible on the surface, likely due to their smaller lateral size and the resolution limitations of the FE-SEM instrument. In the case of f-NS/PU, numerous nanosheets are visible in the centres of the spherulitic domains, attributed to their significantly larger lateral dimensions (> tens of microns).

S3. HR-TEM images of p-NS/PU composite films



TEM and HR-TEM images of microtome sectioned p-NS/PU composite depict the uniform distribution of p-NS filler within the PU matrix

Figure S3. Microstructural characterization of neat PU and TiB₂/PU composites at 2 wt.% loading. (a) TEM image of microtome sectioned p-NS/PU composite, which is (b) Zoomed-in view to depict the uniform distribution of p-NS filler in PU matrix; here dashed yellow circles indicate the presence of p-NS filler, (c) HR-TEM image of p-NS/PU composites after adding 2 wt. % nanofillers, here dashed yellow circles represent the intact hexagonal arrangement, and the inset shows a zoomed-in view of such arrangement, the white box represents the region of interest (ROI), selected for calculation of d-spacing (d) The zoomed-in image of ROI, represent (100) plane of TiB₂.

In order to assess how these TiB_2 fillers are distributed in the PU matrix, HRTEM imaging was carried out on microtome-sectioned p-NS/PU nanocomposites, as shown in figure S3. We observed dark and bright domains and some continuous fringes (Figure S3a).¹ Mondal et al. also observed such segregated domains, which demonstrated the incompatibility of hard

and soft segments in melted form.² In addition, continuous fringes represent the presence of crystalline nanosheets in the PU matrix, as evidenced by XRD patterns in Figure 2h.

The zoomed-in view of the TEM image (Figure S3a) indicates the uniform distribution of pristine nanosheets in the PU matrix (Figure S3b). In this image, dashed yellow circles indicate the presence of p-NS filler. The HR-TEM image of p-NS/PU nanocomposites (Figure S3c) shows fringes, indicating the nanosheet's intact crystallinity during composite formation and retained hexagonal arrangement. The advantage of the retained native lattice is explained later in detail. We also utilized a section from Figure S3c (shown in the white box) to calculate the d-spacing of nanosheets embedded in the polymer matrix. We obtained a d-spacing of 0.25 nm, which corresponds to the (100) plane of TiB₂ (figure S3d)





Figure S4: DMA results of neat PU and p-NS/PU composites. (a) Storage modulus, (b) Loss modulus, and (c) Tan delta (δ).

The thermomechanical response of neat PU and p-NS/PU composite is shown in Figure S4, also confirms the uniform distribution of nanofillers in the PU matrix. We have studied the thermomechanical behaviour of neat PU and p-NS/PU composite. In figure S4(a-c), we have shown the storage modulus (E'), loss modulus (E''), and loss tangent (Tan δ), which are temperature dependent properties. Figure S4a exhibits three temperature dependent regions—(a) low temperature glassy region, (b) narrow steep region, which corresponds to the relaxation in the polymer chains (c) high temperature rubbery plateau.

We found that E' value of neat PU and p-NS/PU composite is very similar in the initial two region. However, as we have shown in the enlarged graph in the inset of Figure S4a, that the E' value is slightly higher as compared to neat PU. The increment in E' value of the nanocomposite is attributed to the restricted movement of the polymeric chain in the presence of uniformly distributed nanosheets; TEM images also corroborate this inference. The Loss modulus curve, as shown in Figure S4b, depicts no change in a composite curve as compared

with neat PU. This suggests that TiB_2 nanofillers do not affect the viscous response of the PU polymer. Further, the damping factor (Tan δ), shown in Figure S4c, mainly remained unchanged even for composites, confirming the uniform presence of nanofillers.



S5. XPS spectra of neat PU and p-NS/PU composite

Figure S5. XPS survey scan of neat PU and p-NS/PU composite

To determine the chemical interaction of TiB₂-based fillers with the PU matrix, we collected XPS data of neat PU and p-NS/PU composite film as shown in Figure S5. XPS spectra of neat PU exhibit the presence of C1s, O1s and N1s peaks (Figure S6). However, in the case of p-NS/PU nanocomposite film, the C1s, O1s, and N1s peaks appear similar to neat PU peaks, and the signals of Ti and B did not appear. This might be because of the very low content of p-NS in the PU matrix (Figure S7).



Figure S6. XPS Spectra of neat PU. (a) N1s spectra, (b) C1s spectra, and (c) O1s spectra.



Figure S7. XPS Spectra of p-NS/PU composite. (a) N1s spectra, (b) C1s spectra, (c) O1s spectra, (d) Ti 2p spectra, and (e) B1s spectra.

S6. Mechanical properties of neat PU and TiB_2/PU composite films

Table S1: Mechanical properties of neat polyurethane (PU) and TiB_2/PU composite at different wt.%.

Samples	wt. %	Young's	Young's Ultimate		Toughness,
		Modulus,	Tensile	break, ε _B (%)	T (MJ/m ³)
		Y (MPa)	strength,		
			UTS (MPa)		
Neat PU	0	20.85±4.82	14.88±3.82	566.67±83.17	48.06±9.72
b-TiB ₂ /PU		21.90±2.71	19.72±6.27	545.33±137.07	59.25±29.09
p-NS/PU	0.5	23.51±4.10	19.20±3.47	496±86.06	54.70±15.18
f-NS/PU		25.44±0.93	$17.60{\pm}5.20$	448±74.08	46.00±17.15
b-TiB ₂ /PU	1	22.35±1.61	21.47±6.65	588±226.24	73.00±47.10
p-NS/PU	1	24.00±2.52	20.84±2.28	582.67±60.57	66.31±10.85

f-NS/PU		26.82±2.02	$19.04{\pm}1.62$	477.33±28.37	49.19±5.91
b-TiB ₂ /PU		25.00±2.8	21.76±1.89	601.33±44.24	69.05±8.11
p-NS/PU	1.5	24.30±4.45	21.78±1.45	509.33±30.02	59.99±6.20
f-NS/PU		25.77 ± 0.8	$15.05{\pm}1.93$	433.33±52.81	39.31±7.34
b-TiB ₂ /PU		23.39±3.48	18.61±2.57	510.67±47.72	54.01±8.86
p-NS/PU	2	24.43±3.20	26.55±2.79	601.33±118	86.14±25.44
f-NS/PU		29.81±2.77	16.96±1.48	430.67±4.62	44.99±3.14
p-NS/PU	5	28.12±8.14	23.50±2.98	582.67±86.00	72.65±8.74

Table S2: A summary of the mechanical properties obtained using differentnanofillers/polyurethane-based composites.

Polymer	filler	Method of	wt.		% increase		
matrix		preparatio	%/v%	Young's	Ultimat	Toughness	\$
		n		Modulus	е	, T	
				,	Tensile	(<i>MJ/m</i> ³)	
				Y (MPa)	strength		
					, <i>UTS</i>		
					(MPa)		
Polyurethane	TiB_2 -based	Solution	2	17	80	80	Present
	pristine	casting					work
	nanosheets						
Polyurethane	Liquid metal-	Vacuum	30	60	65	157	3
	based nano	filtration					
	assemblies						
Polyurethane	Tannic acid-	Vacuum	16	188	700	1539	4
	based WS2	filtrations					
Waterborne	Metal-	Simple	2.5		195		5
polyurethane	organic	mixing					
	framework						
Polyurethane	Carbon	Solution	0.2	68	21	46	6
	nanotubes	casting					
hyperbranche	graphene	solution	2	130	130	170	7
d	oxide	casting					
polyurethane							
Waterborne	c-MoS ₂	solution	1.25(v%	85	140		8
polyurethane		casting)				

Thermoplastic polyurethane	Organophilic graphene nanosheets	solution casting	0.5	230	165	800	9
Polyurethane	MXenes	Vacuum filtration	20		570	-97	10
Thermoplastic polyurethane	Polydopamin e f- graphene nanoplatelets	solution casting	0.5	68	313	279	11
Thermoplastic polyurethane	graphene nanoribbons	solution casting	0.5	77	12.5		12
Polyurethane	amine-f graphene oxide (f-GO)	solution casting	2	123	-30		13

S7. FE-SEM images of neat PU and TiB₂/PU composite films (after fracture morphology)



Figure S8. Microstructural characterization of fractured surface of neat PU and TiB_2/PU composites at 2 wt.% loading. FE-SEM images of (a) neat PU, (b) b- TiB_2/PU , (c) p-NS/PU, and (d) f-NS/PU composite depict voids on the surface of the composite.

S8. Equilibration of molecular dynamics models

A long NPT equilibration was performed for all the model structures. For neat PU and TiB_2 ns/PU composites, the equilibrium density was achieved after an NPT equilibration of 2 ns as shown in the plots below. These equilibrated structures were then used for the tensile simulations.



Figure S9. (a) Neat PU, (b) 1 wt.% $TiB_2 ns/PU$ composite, (c) 4 wt.% $TiB_2 ns/PU$ composite, and (d) 8 wt.% $TiB_2 ns/PU$ composite.

S9. Mechanical properties of neat PU and TiB₂/PU composite films obtained through simulations

Table S3: Consolidated mechanical properties of five models

Model	weight	Density	Young's	Yield	Ultimate	Percentage of
	fraction	in g/cc	modulus	Strength	Tensile	strain at failure
			(MPa)	(MPa)	Strength, UTS	(%)
					(MPa)	
Neat PU	0	0.91	613.66	19.50	77.42	700
TiB ₂ -	1	1.01	685.62	19.72	82.45	340
NS/PU	2	1.04	698.51	20.42	76.98	370
	4	1.06	725.86	19.72	92.23	345

S10. Anisotropic nature of load-bearing in neat PU and composites

We have shown the stress-strain curves for neat PU and TiB₂-NS/PU composites in the *x*, *y*, and *z* directions in the figure below. These figures depict the anisotropic behaviour of neat PU, which seems to become isotropic with increasing wt.% of TiB₂ nanosheets in the PU matrix. Snapshots corresponding to these structures at a strain of 3 are also depicted.



Figure S10: Stress-strain curves and corresponding crazing of PU at a strain of 3 along x, y and z-directions while tensile testing for neat PU, 4wt.% and 8wt.% TiB₂-NS based composite.

S11. FTIR band assignment

Table S4: FTIR band assignment of neat PU and TiB_2/PU composite film

Assignment of hand	Wavenumber (cm ⁻¹)				
Assignment of band	Neat PU	b-TiB ₂ /PU	p-NS/PU	f-NS/PU	
Hydrogen-bonded N-H stretching	3330	3330	3327	3334	
Asymmetric CH ₂ stretching	2959	2958	2958	2959	
Free C=O stretching	1729	1723	1721	1727	

N-H band primary amines	1596	1594	1590	1596
C-N stretching	1526	1526	1519	1527

S12. Calculation of Hydrogen bonding index (HBI) and degree of phase separation

The hydrogen bonding index (HBI) was derived by calculating the ratio of the H-bonded carbonyl group (C=O, 1699 cm⁻¹) and the free carbonyl group (C=O, 1730 cm⁻¹). The degree of phase separation is calculated by dividing the ratio of the area of the carbonyl group (C=O, 1699 cm⁻¹) by the total area of the free and H-bonded carbonyl group.¹⁴



Figure S11: Carbonyl stretching region from FTIR spectra, which is used for the calculation of HBI.

S13. Cross-sectional FE-SEM images of the fractured surface of neat PU and TiB_2/PU composites at 2 wt. % loading



Figure S12. Cross-sectional FE-SEM images of the fractured surface of (a) neat PU, (b) b-TiB₂/PU composite, (c) p-NS/PU composite, and (d) f-NS/PU composite.

S14. Cross-sectional FE-SEM images of the fractured surface of p-NS/PU composite at different wt.%.



Figure S13. Cross-sectional FE-SEM images of the fractured surface of (a) neat PU, and p-NS/PU composites at (b) 0.5wt.%, (c) 1 wt.%, (d) 1.5 wt.%, (d) 2 wt.%, (e) 5 wt.%. It depicts an increased number of nanosheets at the fractured surface with increasing wt. fraction.

S15: Thermal properties of neat PU and TiB₂/PU composite

Samples	T _{10%} (°C)	T 90% (°C)	Residue at 600 °C (wt. %)
Neat PU	328	448	1.08
b-TiB ₂ /PU	342	482	5.26
p-NS/PU	312	482	6.05
f-NS/PU	310	420	0

Table S5: TGA data of the PU and PU/TiB ₂ -based nanocomposite at 2 w	rt. % loading
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Table S6: DSC data of the PU and TiB₂-based nanocomposite at 2 wt. % loading

Samples	T_{g}	T_{m1}	T_{m2}	ΔH (J/g)	% Crystallinity (χ _c)
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Neat PU	-40.4	70.6	156.6	4.28	2.76
b-TiB ₂ /PU	-40.1	68.4	156.25	12.01	7.91
p-NS/PU	-36.4	70.2	158.5	5.28	3.48
f-NS/PU	-35.5	70.6	161.4	6.17	4.06

We calculated the % crystallinity (χ_c), using the formula mentioned below

$$\chi_c = \frac{\Delta H}{(1-m) * \Delta H^0}.$$
(3)

Here,

 $\chi_c = \% \ crystallinity$

 ΔH = Enthalpy of fusion (J/g)

 ΔH^0 = Enthalpy of fusion for 100% crystalline PU (J/g), it is taken as 155 J/g as reported previously.¹⁵

m = weight fraction of the filler

S16. Crystal structure of Titanium diboride (TiB₂):



Figur

e S14. (a) Representation of P6/mmm crystal structure of TiB_2 , the yellow colour sphere represents the titanium atom, and the dark red colour sphere represents the boron atoms, arranged in a hexagonal manner between the titanium atoms, (b) A unit cell of TiB_2 .¹⁶

S17. Preparation of TiB₂/PU composites

The following table lists the proportions of PU, DMF and TiB_2 -based filler to obtain TiB_2/PU composites. We prepared the composites by maintaining an equal weight (600 mg) and equal volume (30 mL) of TiB_2/PU dispersion.

Table S7: Quantitative proportions of TiB_2 filler, solvent and polymer for composites preparation.

S.no.	Volume of melt PU solution added (mL)	Volume of DMF added (mL)	Amount of TiB ₂ added (mg)	Final wt.% of TiB ₂ filler in composite
1.	8	22	0	0
2.	7.96	22.04	3	0.5
3.	7.92	22.08	6	1
4.	7.88	22.12	9	1.5
5.	7.84	22.16	12	2
6.	7.6	22.4	30	5

S18. Details of the molecular weight of polyurethane (PU) used in this study



Figure S15. Molecular weight of polyurethane (PU) measured using Gel permeation chromatography (GPC)

S19. Details regarding the functional form of the Pcff+ class 2 force field

In our simulations, we initially modelled PU chain [1] using MedeA [2] package and performed energy minimisation on the periodic replica of single chain PU using pcff+ force field parameters (polymer consistent force field). The pcff+ is a class 2 force field comprised of the following functional terms that describe the total potential energy of the system.

Lj/class2 potential

$$E = \varepsilon \left[2 \left(\frac{\sigma}{r} \right)^9 - 3 \left(\frac{\sigma}{r} \right)^6 \right], r < r_c$$

Where r_c is cutoff distance, ϵ and σ are energy and distance.

Bond Style potential

$$E = K_2(r - r_0)^2 + K_3(r - r_0)^3 + K_4(r - r_0)^4$$

K terms are energy/distance^{2,} and r_0 is distance

Angle style potential

$$E = E_{a} + E + E_{\beta a}$$

$$E_{a} = K_{2}(\theta - \theta_{0})^{2} + K_{3}(\theta - \theta_{0})^{3} + K_{4}(\theta - \theta_{0})^{4}$$

$$E_{\beta\beta} = M(r_{ij} - r_{1})(r_{jk} - r_{2})$$

$$E_{\beta\alpha} = N_{1}(r_{ij} - r_{1})(\theta - \theta_{0}) + N_{2}(r_{jk} - r_{2})(\theta - \theta_{0})$$

 θ_0 is angle, K_2 to K_4 are energies in eV

Dihedral style potential

$$\begin{split} E &= E_{a} + E_{\beta\beta} + E_{\beta a} + E_{at} + E_{aat} + E_{\beta\beta13} \\ E_{a} &= \sum_{n=1^{3}} K_{n} [1 - \cos(n\varphi - \varphi_{n})] \\ E_{\beta\beta=} & (r_{jk} - r_{2}) [A_{1}cos(\varphi) + A_{2}cos(2\varphi) + A_{3}cos(3\varphi)] \\ & (r_{ij} - r_{1}) [B_{1}cos(\varphi) + B_{2}cos(2\varphi) + B_{3}cos(3\varphi)] + (r_{kl} - r_{3}) \\ E_{\beta\alpha=} & [C_{1}cos(\varphi) + C_{2}Cos(2\varphi) + C_{3}Cos(3\varphi)] \\ & (\theta_{ijk} - \theta_{1}) [D_{1}cos(\varphi) + D_{2}cos(2\varphi) + D_{3}cos(3\varphi)] + (\theta_{jkl} - \theta_{2}) \\ E_{\alphat=} & [E_{1}cos(\varphi) + E_{2}cos(2\varphi) + E_{3}cos(3\varphi)] \\ & E_{\alpha\alphat=M}(\theta_{ijk} - \theta_{1})(\theta_{jkl} - \theta_{2})cos(\varphi) \\ & E_{\beta\beta13=N} (r_{ij} - r_{1}) (r_{kl} - r_{3}) \end{split}$$

Here, K, D, M and E terms are energy, φ terms are angles, A, B and C terms are energy/distance, N is energy/distance², and r is distance.

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