Optimized Gradient Coatings and the Unexplored Potential of Reverse Gradient Coating Designs

Ayse Cagil Kandemir, Hatice Kaplan Can

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Background & Motivation

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- Surface coatings critical in biomedical & structural applications
- **Gradient structures** mimic biological systems (e.g. fish armor, bone, nacre shell)
- **Aim:** Improve mechanical performance of biocompatible composites.

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PROGRESS IN ORGANIC COATINGS

Impact of gradient nanocomposite coating design on the surface mechanical properties of soft composite substrate

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ABSTRACT

This study examines the influence of gradient nanocomposite coatings on the surface mechanical properties of soft composite substrates (modulus: 150 MPa). Polyvinylpyrrolidone reinforced with halloysite nanotubes was used to fabricate gradient (e.g. 5/15/30 wt%) and reverse gradient (e.g. 30/15/5 wt%) coatings for comparative analysis. Reverse gradient coatings consistently exhibited superior surface properties, particularly in thicker (30 μm) systems, where stiffer sublayers effectively transferred stress to the surface. The 30/15/5 reverse gradient coating achieved a modulus of 2.92 GPa, significantly outperforming its gradient counterpart (0.33 GPa) at similar indentation depths. In contrast, thinner (15 μm) gradient coatings with smaller concentration variations (5/10/15 wt%) facilitated a significantly smoother mechanical transition and improved stress distribution, while larger concentration differences (5/15/30 wt%) amplified substrate effects, increasing indentation depth. These findings highlight the trade-offs in coating design: gradient coatings optimize mechanical transitions, making them ideal for functional interfaces and load-distributing layers, while reverse gradient coatings ensure greater mechanical consistency, making them suitable for protective and structural applications requiring enhanced surface durability.

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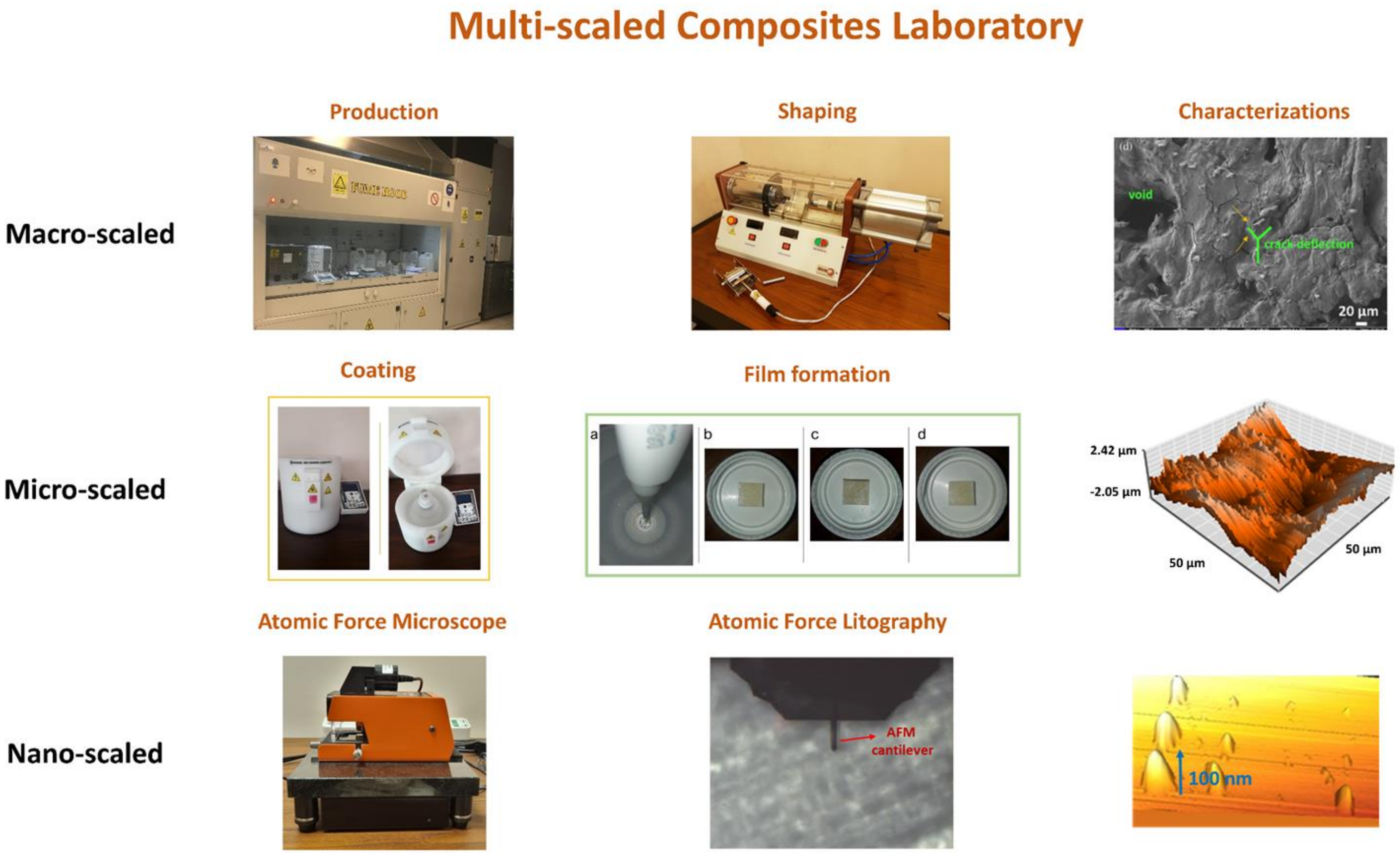

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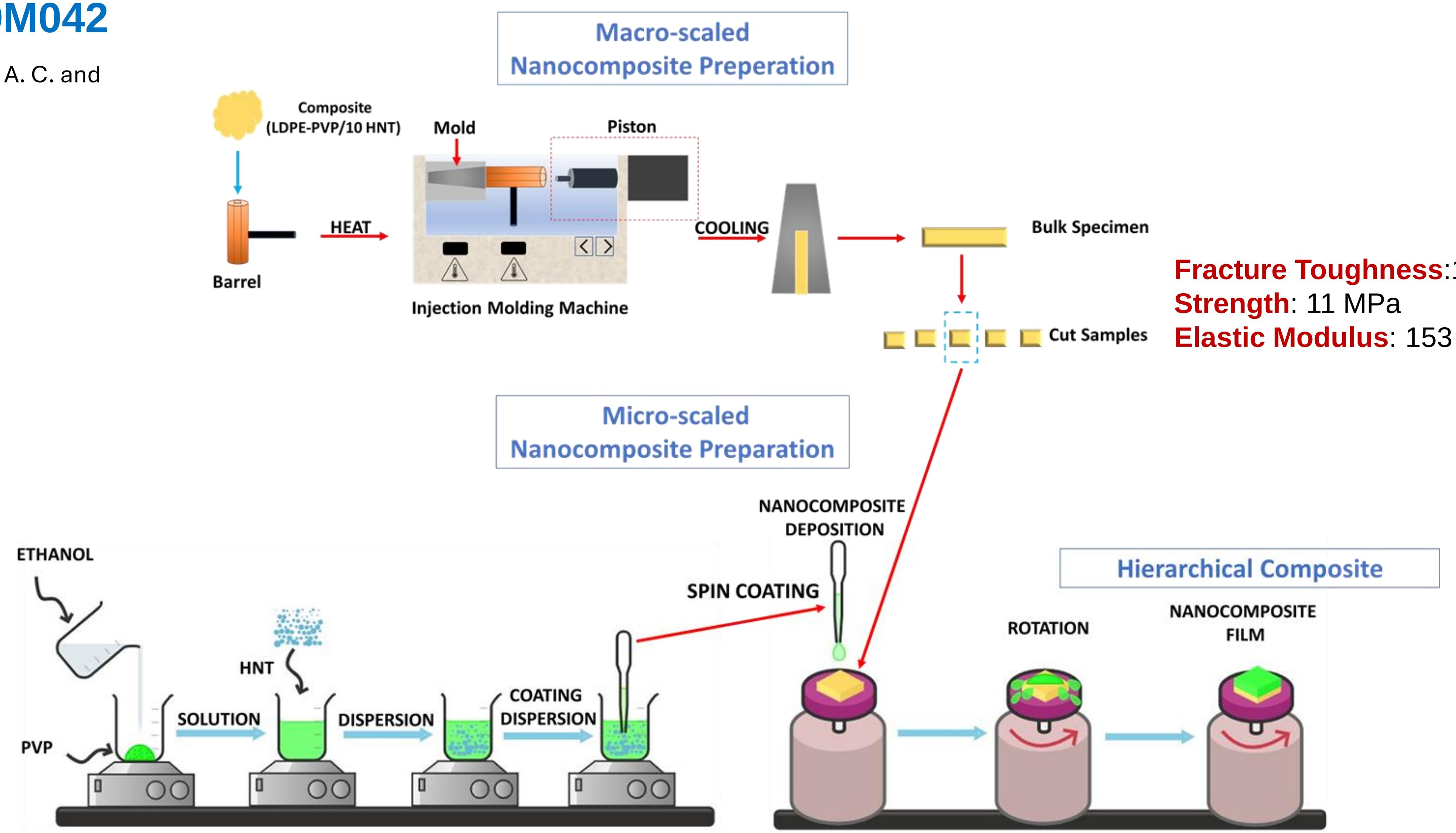
TÜBİTAK 3501-119M042

Patent 2024/003959 TR –Kandemir A. C. and Can H. K 2024.



Fracture Toughness:18 kJ/m2
Strength: 11 MPa
Elastic Modulus: 153 MPa

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- **Matrix:**

Polyvinylpyrrolidone (PVP)

- **Reinforcement:**

Halloysite nanotubes (HNTs)

- **Fabrication:**

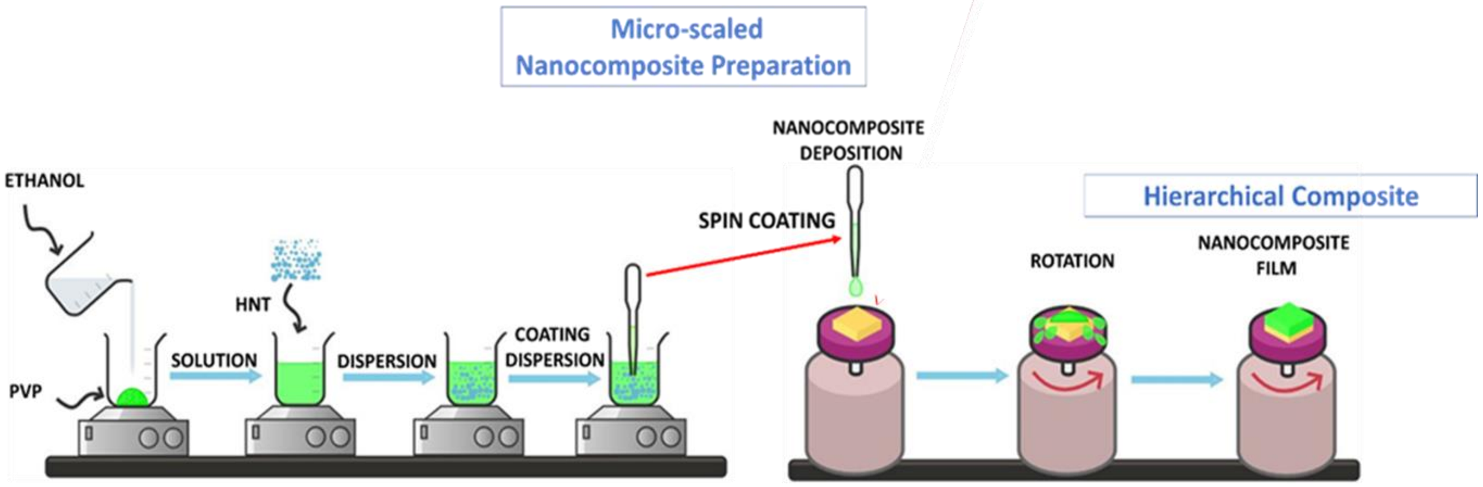
Solvent mixing + spin coating

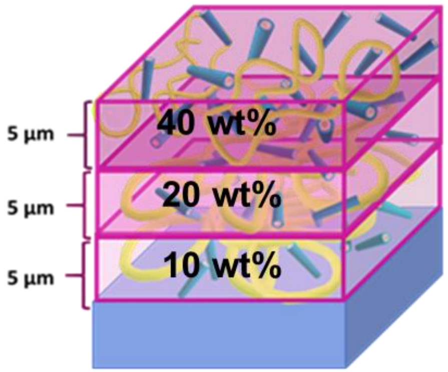
- **Characterization:**

AFM, TEM

- **Mechanical Behavior:**

Instrumented-indentation





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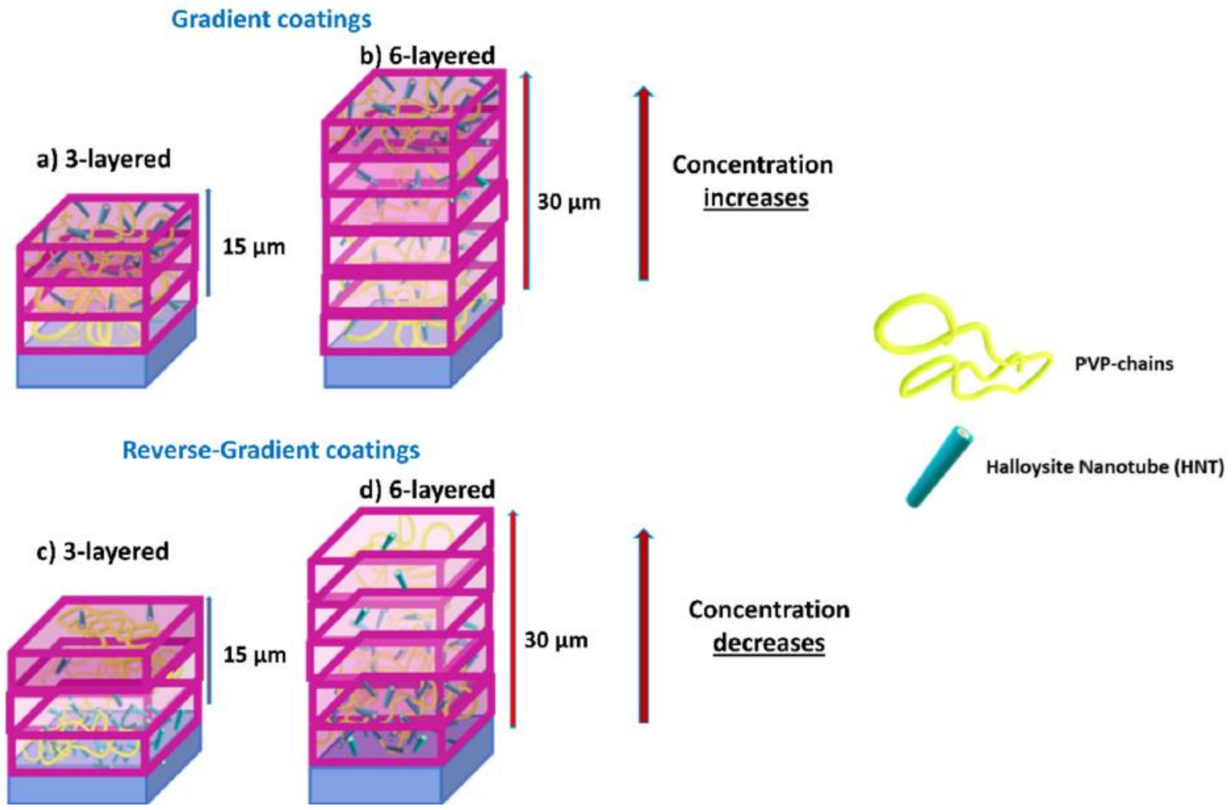
Coating Configurations

- **Gradient:** HNT wt% increases top-down (e.g., 5/15/30)
- **Reverse Gradient**: HNT wt% decreases top-down (e.g., 30/15/5)
- **Thickness:**

✓ **Thin:**15 µm (3-layer)

✓ **Thick**: 30 µm (6-layer)



Pristine Coatings

- **Glass substrate:**

E=70 GPa

Thickness: 15 µm (3-layer)

- **Composite Substrate:**

E=150 MPa

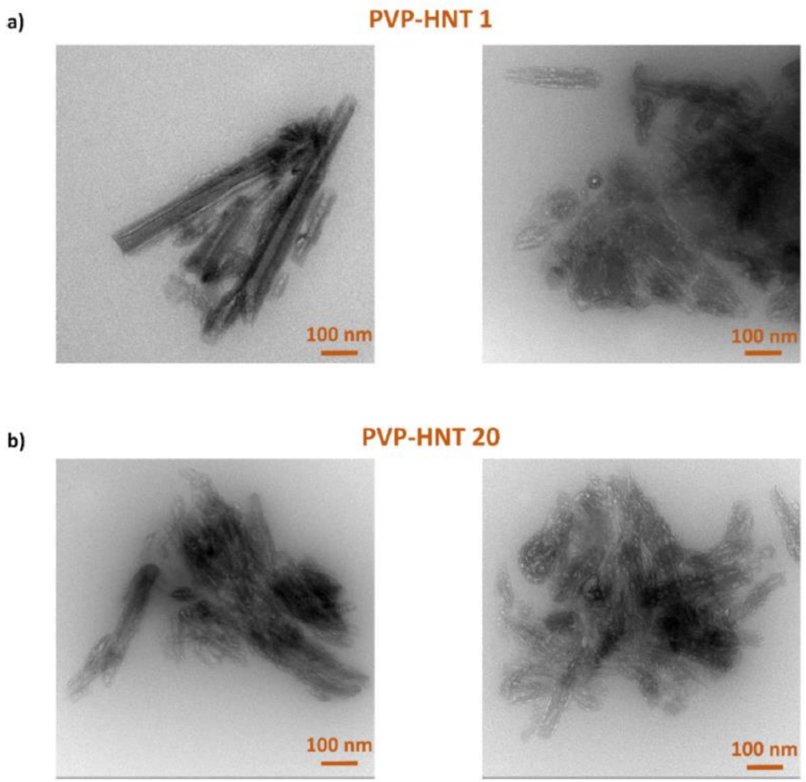
Thickness: 15 µm (3-layer)

Designation and HNT composition of pristine nanocomposite films (15 µm thickness).

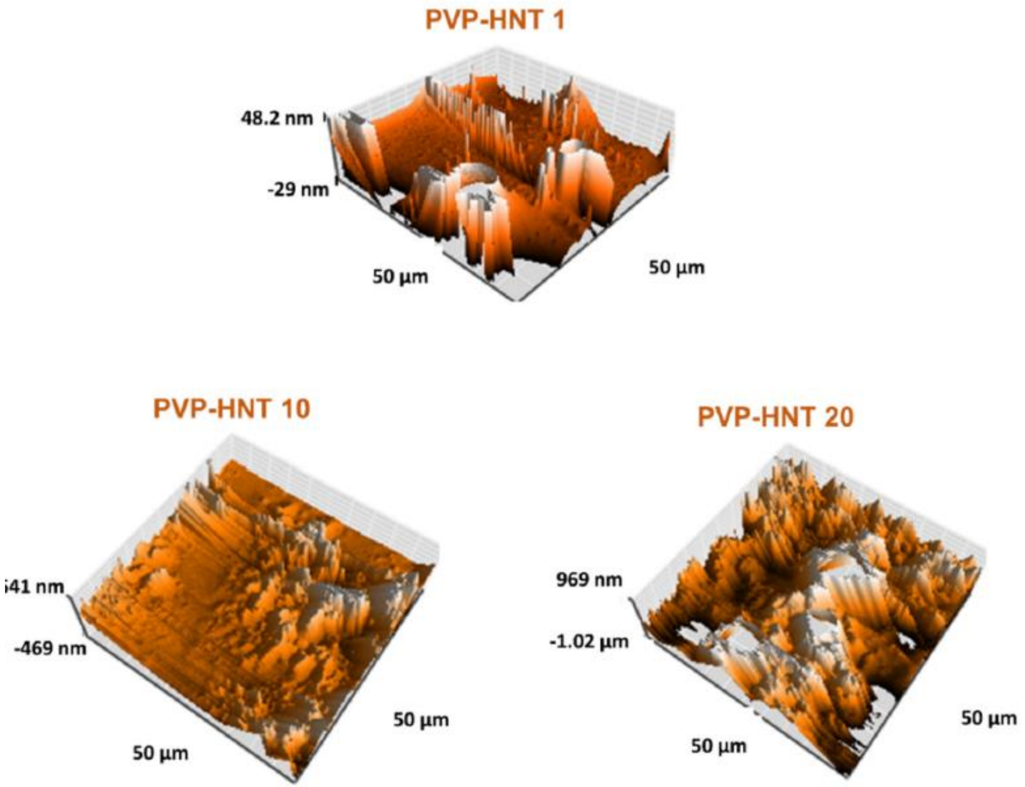
Samples	HNT (wt%)	HNT (vol%)
PVP	–	–
PVP-HNT 1	1	0.5
PVP-HNT 3	3	1.5
PVP-HNT 5	5	2.5
PVP-HNT 10	10	5
PVP-HNT 15	15	7.5
PVP-HNT 20	20	10
PVP-HNT 30	30	15

Pristine Coatings

TEM



AFM



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Pristine Coatings

Instrumented-indentation

Maximum Load: 2 mN

Glass substrate

Samples	Hardness (GPa)	Elastic modulus (GPa)	Maximum indentation depth (nm)
PVP	0.456 ± 0.063	9.30 ± 1.05	444.95 ± 38.12
PVP-HNT 1	0.703 ± 0.141	6.88 ± 0.18	451.49 ± 26.53
PVP-HNT 3	0.583 ± 0.192	32.43 ± 11.49	415.13 ± 62.98
PVP-HNT 5	0.555 ± 0.141	18.77 ± 3.57	431.89 ± 49.83
PVP-HNT 10	0.786 ± 0.362	18.56 ± 7.23	413.14 ± 135.50
PVP-HNT 15	0.530 ± 0.164	16.95 ± 5.22	452.58 ± 75.46
PVP-HNT 20	1.670 ± 0.641	38.54 ± 5.73	425.50 ± 47.48
PVP-HNT 30	3.153 ± 0.543	44.05 ± 8.81	362.70 ± 18.44

Composite substrate

Samples	Hardness (GPa)	Elastic modulus (GPa)	Maximum indentation depth (nm)
PVP-HNT 5	0.785 ± 0.042	3.76 ± 0.12	537.78 ± 8.15
PVP-HNT 10	0.584 ± 0.211	5.40 ± 0.11	523.94 ± 63.43
PVP-HNT 15	0.532 ± 0.102	10.96 ± 0.68	461.01 ± 31.82
PVP-HNT 30	0.518 ± 0.106	19.31 ± 4.87	444.44 ± 41.01

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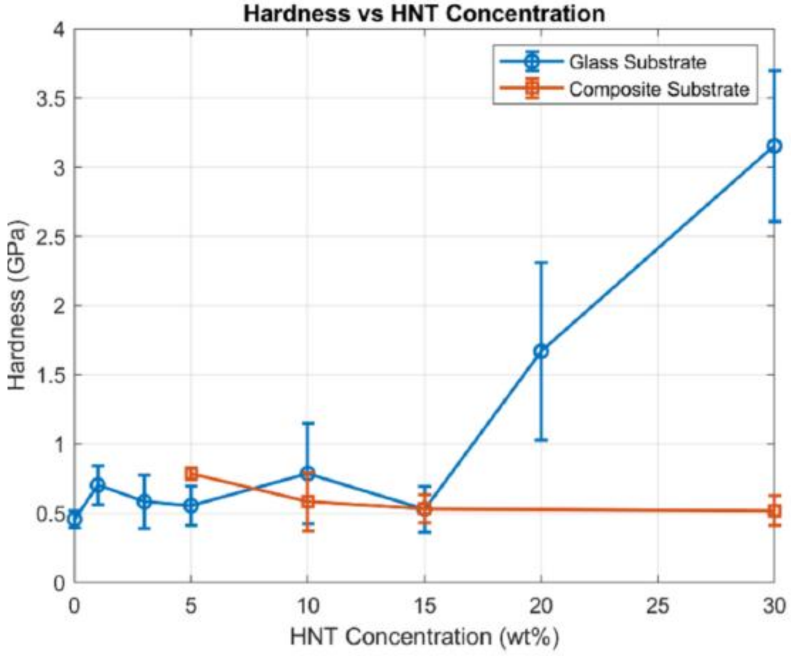
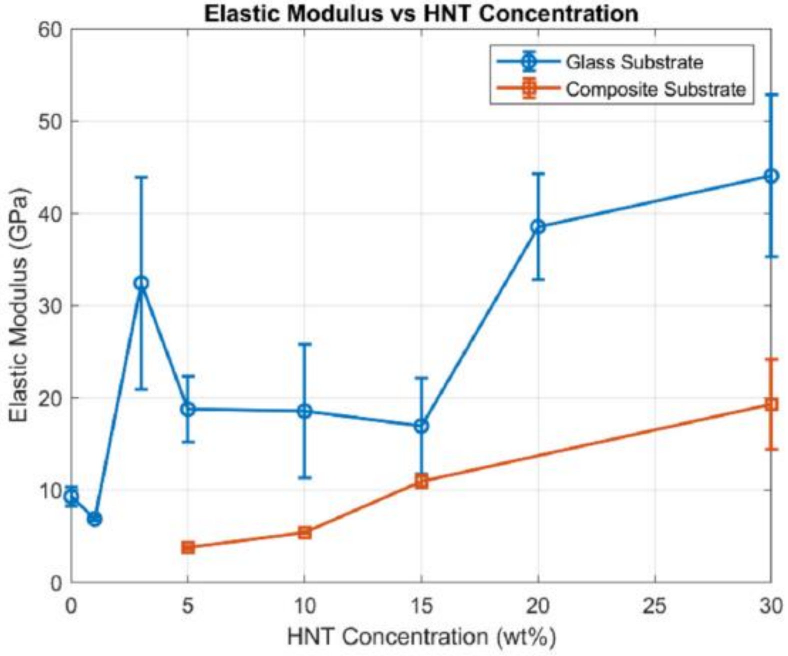
Pristine Coatings

Instrumented-indentation

Maximum Load: 2 mN





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Pristine Coatings

Instrumented-indentation

•**Rigid (glass) substrates:**

- Hardness increases up to **3.15 ± 0.54 GPa**
- Elastic modulus reaches **44.05 ± 8.81 GPa**

•**Soft composite substrates**

- Hardness remains nearly **constant** across HNT concentrations
- Modulus peaks at **19.31 ± 4.87 GPa** for 30 wt% HNT

✓ Despite lower values on soft substrates, **indentation depths (400–500 nm)** are similar across both surfaces at 2 mN load.

✓ Indicates **force is well-distributed** even in compliant substrates without severe deformation.

✓ Emphasizes need to **co-optimize filler distribution and substrate compatibility** for effective nanocomposite design.

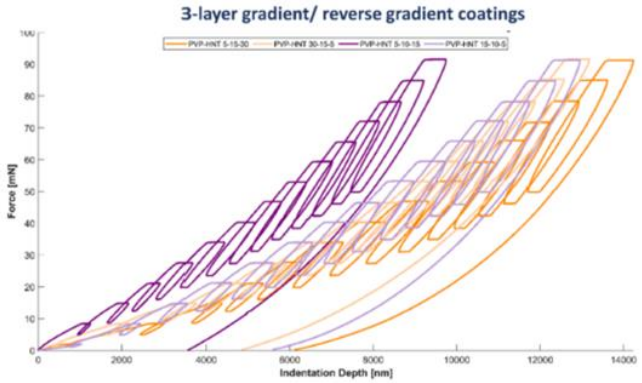
Gradient/ Reverse Gradient Coatings

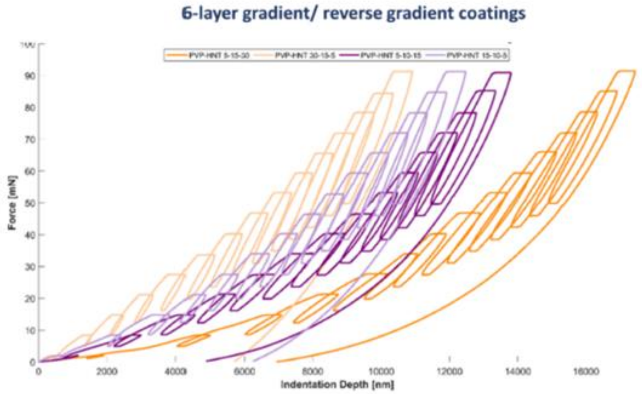
Coating Compositions

Designation and HNT composition of gradient and reverse gradient nano-composite films (each layer corresponds to 5 μm thickness).

Samples	1st layer HNT (wt%)	2nd layer HNT (wt%)	3rd layer HNT (wt%)	4th layer HNT (wt%)	5th layer HNT (wt%)	6th layer HNT (wt%)
5-15-30 PVP-HNT (3 layers)	5	15	30	–	–	–
30-15-5 PVP-HNT (3 layers)	30	15	5	–	–	–
5-10-15 PVP-HNT (3 layers)	5	10	15	–	–	–
15-10-5 PVP-HNT (3 layers)	15	10	5	–	–	–
5-15-30 PVP-HNT (6 layers)	5	5	15	15	30	30
30-15-5 PVP-HNT (6 layers)	30	30	15	15	5	5
5-10-15 PVP-HNT (6 layers)	5	5	10	10	15	15
15-10-5 PVP-HNT (6 layers)	15	15	10	10	5	5

Cyclic-instrumented-indentation





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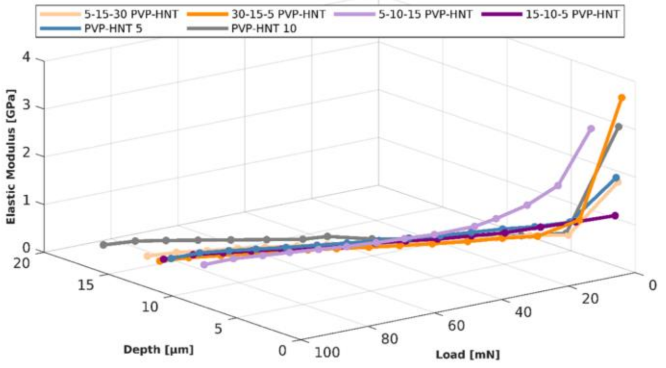
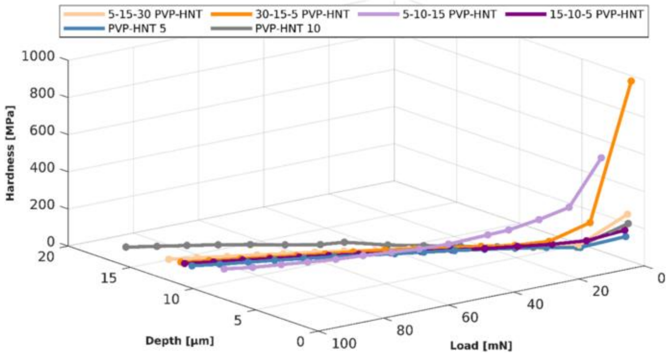
Gradient/ Reverse Gradient Coatings

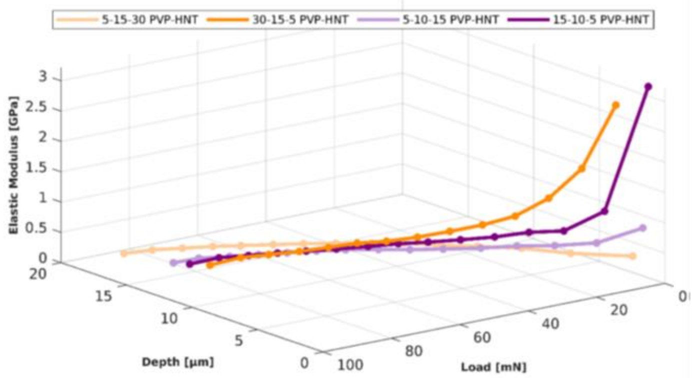
Cyclic-instrumented-indentation

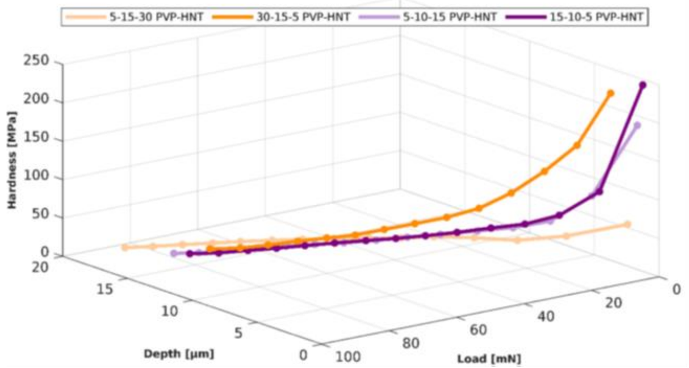
3-layer gradient/ reverse gradient coatings





6-layer gradient/ reverse gradient coatings





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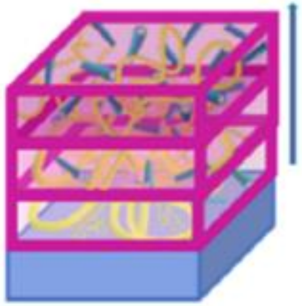
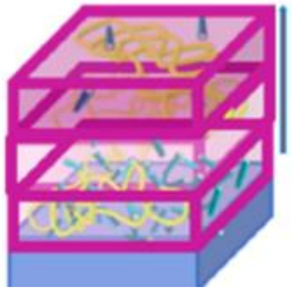
Gradient/ Reverse Gradient Coatings

Thin Coating-3 layers-15 μm

High concentration difference





Gradient

		Test-level	Depth (μm)	Load (mN)	E (GPa)	H (MPa)
(5-15-30 PVP-HNT) 3 layers	1st Layer (30 wt% HNT)	1	0.82	2.03	1.850	266.32
		2	3.01	8.42	0.630	73.04
		3	4.36	14.80	0.586	53.84
	2nd Layer (15 wt% HNT)	4	5.35	21.13	0.531	53.45
		5	6.28	27.71	0.515	49.04
		6	7.27	34.01	0.468	45.42
		7	8.32	40.33	0.426	40.51
		8	9.31	46.88	0.413	36.02
	3rd Layer (5 wt% HNT)	9	10.16	53.22	0.401	33.86
		10	10.90	59.21	0.393	32.46
		11	11.64	66.05	0.392	31.16
		12	12.25	71.77	0.391	30.33
		13	12.93	78.37	0.377	30.40
		14	13.61	85.00	0.370	29.37
		15	14.23	91.26	0.326	29.88

Reverse Gradient

		Test-level	Depth (μm)	Load (mN)	E (GPa)	H (MPa)
(30-15-5 PVP-HNT) 3 layers	1st Layer (5 wt% HNT)	1	0.52	2.02	3.646	989.94
		2	2.15	8.42	1.025	213.03
		3	3.75	14.82	0.627	98.42
		4	4.85	21.11	0.573	73.50
	2nd Layer (15 wt% HNT)	5	5.91	27.43	0.496	65.92
		6	6.95	34.06	0.445	58.33
		7	7.84	40.35	0.414	53.87
		8	8.65	46.44	0.393	50.75
		9	9.41	53.19	0.390	46.48
	3rd Layer (30 wt% HNT)	10	10.04	59.39	0.393	43.97
		11	10.64	65.76	0.392	42.96
		12	11.23	71.98	0.382	42.78
		13	11.87	78.30	0.371	41.66
		14	12.57	85.26	0.360	40.15
		15	13.17	91.61	0.323	41.03

Gradient/ Reverse Gradient Coatings

Thin Coating-3 layers-15 µm

High concentration difference

•**Mechanical performance varies significantly** based on filler gradient direction and layer configuration.

•**Reverse gradient (30→15→5 wt%)** shows superior surface mechanical properties:

- **Elastic modulus**: 3.6 GPa
- **Hardness**: 990 MPa at 0.52 µm depth

•In contrast, the **standard gradient (5→15→30 wt%)** yields:

- **Elastic modulus**: 1.85 GPa
- **Hardness**: 266 MPa at similar depth

•Enhanced response in reverse gradient arises from:

✓ Stiff bottom layers acting as load distributors

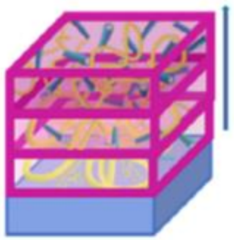
✓ Efficient **stress transfer toward surface** without excessive compliance

•Indicates **reverse gradients outperform in surface reinforcement** even at minimal coating thickness.

Gradient/ Reverse Gradient Coatings

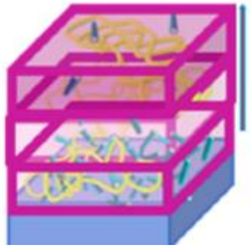
Thin Coating-3 layers-15 µm

Low concentration difference



Gradient

		Test-level	Depth (µm)	Load (mN)	E (GPa)	H (MPa)
(5-10-15 PVP-HNT) 3 layers	1st Layer (15 wt% HNT)	1	n.a	n.a	n.a	n.a
		2	1.25	8.42	3.020	582.75
		3	2.16	14.80	1.834	317.62
		4	2.92	21.12	1.442	256.60
		5	3.67	27.52	1.182	205.85
		6	4.44	34.01	0.997	173.83
	2nd Layer (10 wt% HNT)	7	5.16	40.29	0.890	140.02
		8	5.79	46.83	0.840	123.01
		9	6.39	52.97	0.787	113.44
		10	7.01	59.39	0.738	103.21
		11	7.58	65.57	0.714	92.16
		12	8.14	72.07	0.690	86.88
		13	8.66	78.14	0.664	83.18
		14	9.20	84.82	0.642	79.17
		15	9.74	91.51	0.560	82.08



Reverse Gradient

		Test-level	Depth (µm)	Load (mN)	E (GPa)	H (MPa)
(15-10-5 PVP-HNT) 3 layers	1st Layer (5 wt% HNT)	1	1.04	2.04	1.127	175.65
		2	2.45	8.39	0.956	108.81
		3	3.54	14.77	0.835	87.10
		4	4.60	21.28	0.711	73.83
	2nd Layer (10 wt% HNT)	5	5.59	27.52	0.645	61.65
		6	6.54	33.99	0.581	55.75
		7	7.37	40.32	0.555	50.85
		8	8.14	46.46	0.526	47.75
		9	8.95	53.24	0.498	45.09
		10	9.73	59.48	0.474	42.47
	3rd Layer (15 wt% HNT)	11	10.43	65.83	0.460	40.39
		12	11.10	72.22	0.450	38.83
		13	11.73	78.19	0.440	37.47
		14	12.36	84.76	0.436	35.83
		15	12.95	91.31	0.377	37.51

Gradient/ Reverse Gradient Coatings

Thin Coating-3 layers-15 μm

Low concentration difference

In **low concentration difference designs**, performance trend reverses:

•**Gradient (5→10→15 wt%)** shows superior surface mechanics.
At 1.25 μm depth, **gradient coating** achieves:
- ❑ **Elastic modulus**: 3.02 GPa
- ❑ **Hardness**: 583 MPa

•In contrast, **reverse gradient (15→10→5 wt%)** yields:
- ❑ **Elastic modulus**: 1.13 GPa
- ❑ **Hardness**: 176 MPa at At 1.25 μm depth

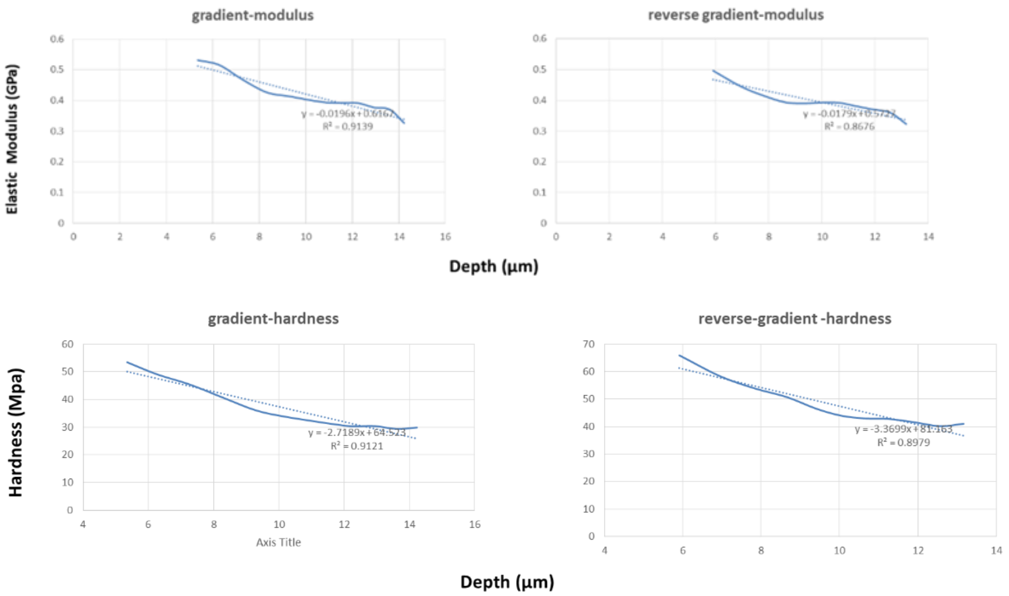
•**Gradient design better distributes mechanical performance** when concentration steps are smaller.

•Results imply **more integrated reinforcement and uniform stress distribution** in subtle gradient configurations.

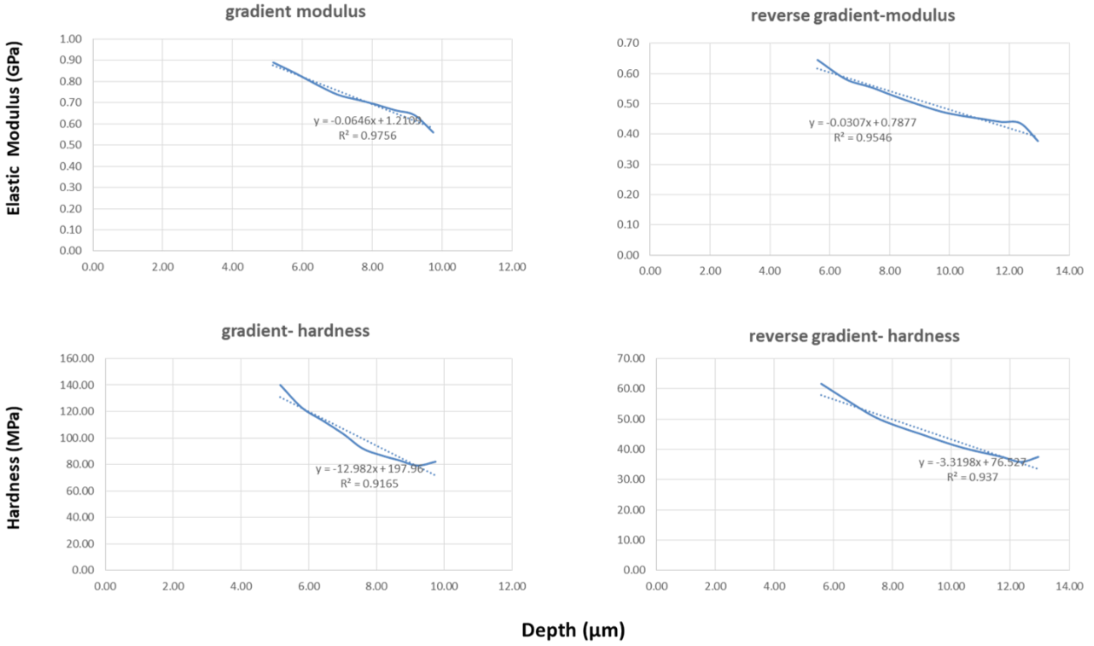
Gradient/ Reverse Gradient Coatings

Thin Coating-3 layers-15 μm

High concentration difference



Low concentration difference



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Gradient/ Reverse Gradient Coatings

30 µm

Thick Coating-6 layers-30 µm

High concentration difference

Gradient

		Test-level	Depth (µm)	Load (mN)	E (GPa)	H (MPa)
(5-15-30 PVP-HNT) 6 layers	1st Layer (30 wt% HNT)	1	1.90	2.06	0.333	59.18
		2	4.98	8.41	0.226	32.01
		3	7.07	14.78	0.227	20.07
		4	8.73	21.28	0.209	19.51
	2nd Layer (15 wt% HNT)	5	10.17	27.71	0.197	18.51
		6	11.06	34.01	0.237	17.11
		7	11.90	40.29	0.242	17.68
		8	12.89	46.87	0.244	17.22
		9	13.67	53.25	0.250	17.29
		10	14.39	59.43	0.252	17.39
		11	15.13	66.05	0.257	17.28
		12	15.72	72.00	0.266	17.20
		13	16.33	78.57	0.267	17.47
		14	16.90	85.14	0.271	17.69
		15	17.43	91.41	0.243	18.51

30 µm

Reverse Gradient

		Test-level	Depth (µm)	Load (mN)	E (GPa)	H (MPa)
(30-15-5 PVP-HNT) 6 layers	1st Layer (5 wt% HNT)	1	n.a	n.a	n.a	n.a
		2	1.55	8.42	2.922	237.65
		3	2.47	14.81	1.880	170.16
		4	3.35	21.13	1.397	136.69
		5	4.26	27.46	1.107	108.97
		6	5.12	33.73	0.969	89.45
		7	5.91	40.27	0.878	78.93
		8	6.66	46.82	0.802	72.21
		9	7.36	53.21	0.755	66.30
		10	7.98	59.40	0.748	60.82
		11	8.57	65.58	0.702	59.11
		12	9.17	71.86	0.664	56.99
		13	9.78	78.37	0.641	54.13
	2nd Layer (15 wt% HNT)	14	10.34	84.45	0.618	52.47
		15	10.90	91.32	0.531	54.08

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Gradient/ Reverse Gradient Coatings

Thick Coating-6 layers-30 µm

High concentration difference

•**Reverse gradient (30→15→5 wt%)** coatings deliver superior surface mechanical performance:
- ❑ **Elastic modulus**: 2.92 GPa
- ❑ **Hardness**: 237.65 MPa at 1.55 µm

•**Gradient (5→15→30 wt%)** coatings show:
- ❑ **Elastic modulus**: 0.33 Gpa
- ❑ **Hardness**: 59.18 MPa at similar depth (1.90 µm)

✓ Reverse gradients effectively **transfer stress from rigid sublayers** to the surface, boosting performance.

✓ Thicker top layers in gradient systems **suppress sublayer contributions**, causing:
- ❑ Lower mechanical performance
- ❑ Greater indentation depths

✓ Supports the **rigid body hypothesis**: overly thick stiff top layers reduce effective stress distribution across the coating.

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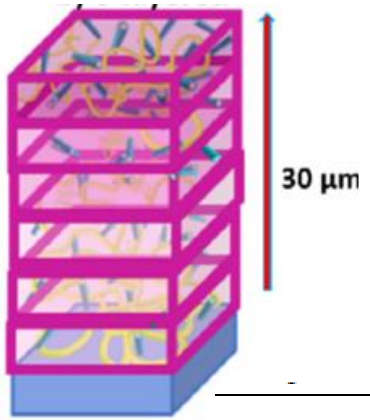
Gradient/ Reverse Gradient Coatings

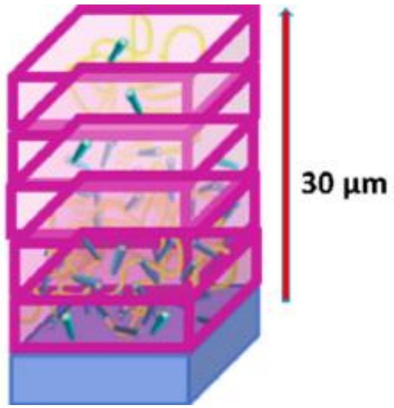


Thick Coating-6 layers-30 µm

Low concentration difference

Gradient

		Test-level	Depth (µm)	Load (mN)	E (GPa)	H (MPa)
(5-10-15 PVP-HNT) 6 layers	1st Layer (15 wt% HNT)	1	1.14	2.06	0.854	192.68
		2	2.99	8.48	0.544	95.77
		3	4.54	14.79	0.457	59.64
		4	5.72	21.30	0.436	50.04
		5	6.87	27.45	0.388	44.50
		6	8.02	34.06	0.361	39.17
		7	8.93	40.37	0.357	36.00
		8	9.73	46.49	0.369	32.83
	2nd Layer (10 wt% HNT)	9	10.47	53.24	0.386	31.14
		10	11.08	59.46	0.389	30.95
		11	11.65	65.83	0.392	31.03
		12	12.22	72.04	0.388	30.89
		13	12.78	78.30	0.390	30.48
		14	13.34	85.21	0.396	29.90
		15	13.79	90.91	0.352	31.33



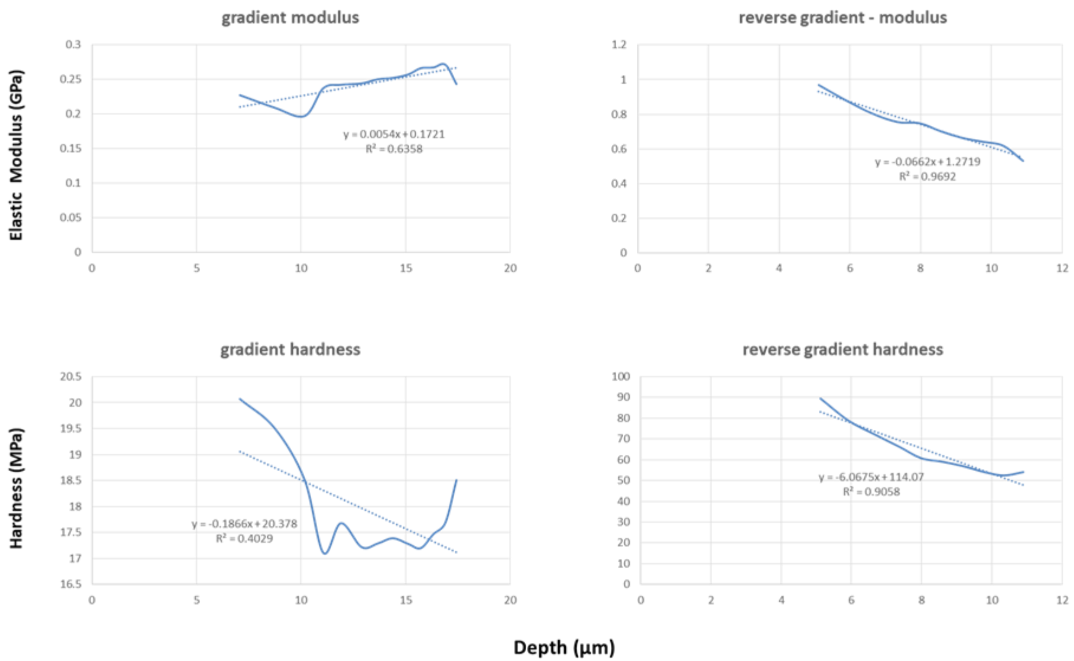
Reverse Gradient

		Test-level	Depth (µm)	Load (mN)	E (GPa)	H (MPa)
(15-10-5 PVP-HNT) 6 layers	1st Layer (5 wt% HNT)	1	0.73	2.03	3.216	247.48
		2	2.40	8.42	1.109	104.59
		3	3.84	14.81	0.751	71.22
		4	4.85	21.13	0.725	59.41
		5	5.80	27.54	0.651	54.55
		6	6.72	34.05	0.609	49.28
		7	7.53	40.34	0.584	45.82
		8	8.22	46.45	0.574	43.66
		9	8.89	52.76	0.551	42.65
		10	9.58	59.39	0.533	41.34
	2nd Layer (10 wt% HNT)	11	10.22	65.73	0.523	39.88
		12	10.78	71.99	0.521	38.75
		13	11.34	78.31	0.513	38.15
		14	11.91	84.77	0.505	37.39
		15	12.46	91.26	0.433	38.85

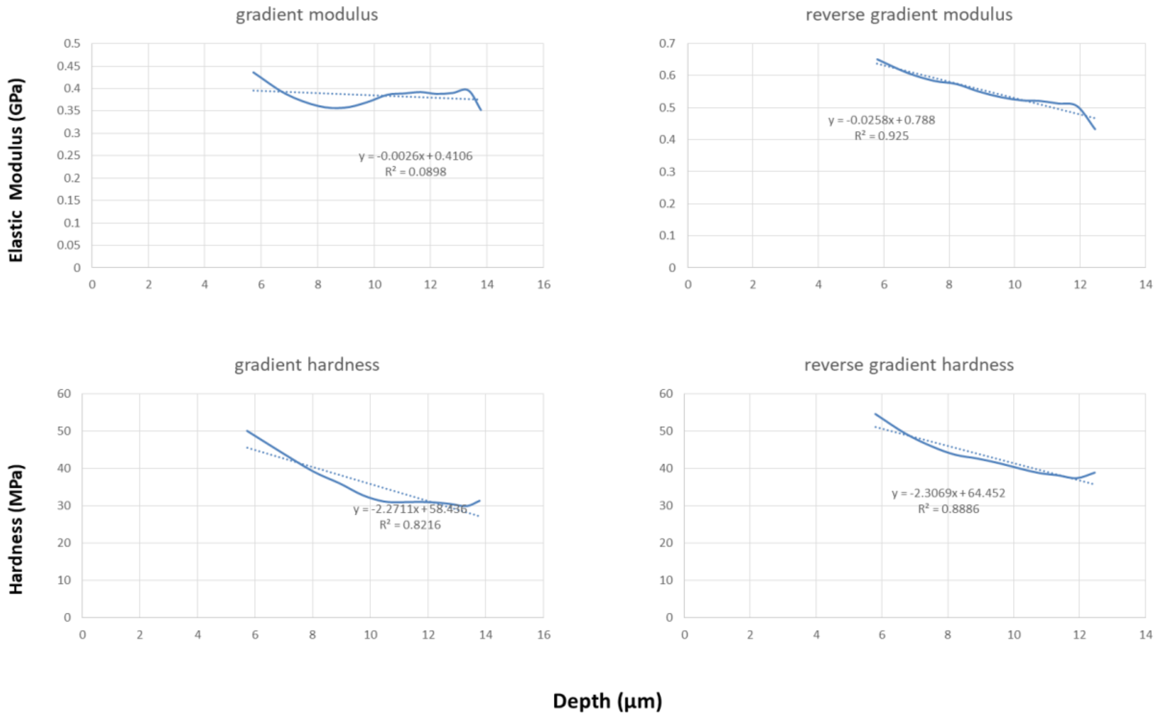
Gradient/ Reverse Gradient Coatings

Thick Coating-6 layers-30 μm

High concentration difference



Low concentration difference



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Conclusions

- Gradient nanocomposite coatings with polyvinylpyrrolidone and halloysite nanotubes were designed for soft composite substrates (150 MPa modulus).

- **Gradient coatings** with **large particle differences** (5/15/30 wt%) restricted stress redistribution, intensifying substrate effects and reducing sublayer contributions.

- **Thinner** (15 μm) **gradient coatings** with **smaller concentration variations** (5/10/15 wt%) improved stress distribution and mechanical transitions, reducing stress concentrations.

- **Reverse gradient coatings** (30/15/5 wt%) exhibited superior surface properties, particularly in thicker (30 μm) coatings, where stiffer sublayers enhanced stress transfer and minimized substrate effects.

- **Gradient coatings are ideal for functional interfaces and load-distributing layers**, while **reverse gradient coatings are better suited for protective and structural applications requiring mechanical stability.**

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