Biomimetic Nanocoatings with Exceptional Mechanical and Barrier Properties for Polyolefin Films

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Nanocoatings from Coassembly of Polymers and Inorganic Nanosheets --- Unique Features

- **Processing**
  - One step co-assembly to form hundreds of layers; very time efficient
  - Very low processing (and raw material) cost and can be processed at conventional coating setup; highly scalable

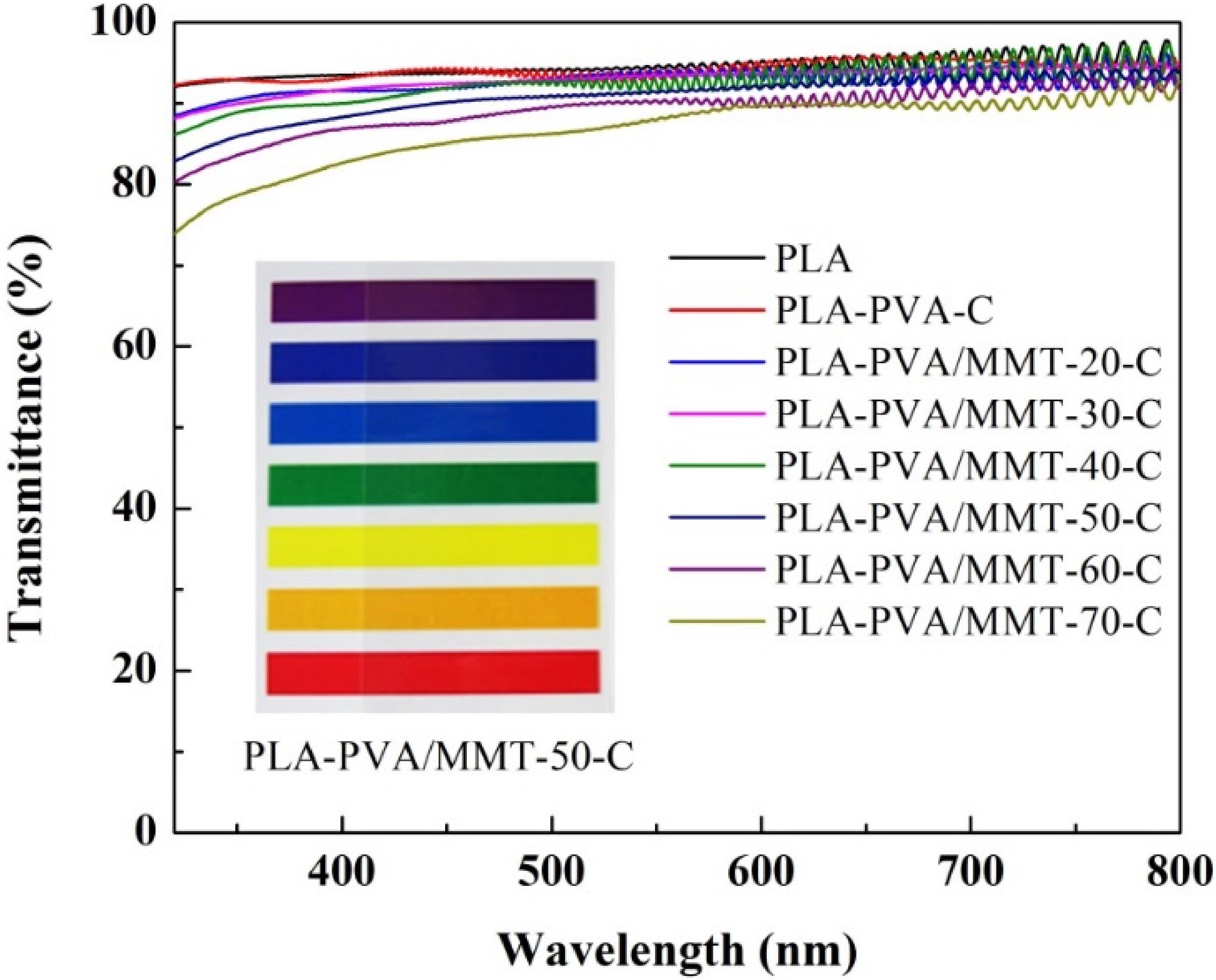
- **Structure**
  - High inorganic loading (up to ~70 wt%) but meanwhile very processable (no viscosity penalty)
  - Highly ordered structure via a facile alignment process
  - Well-integrated into one piece: co-crosslinked (organic-organic crosslinking and organic-inorganic crosslinking)

Nanocoatings from Coassembly of Polymers and Inorganic Nanosheets --- Property *Expectation*

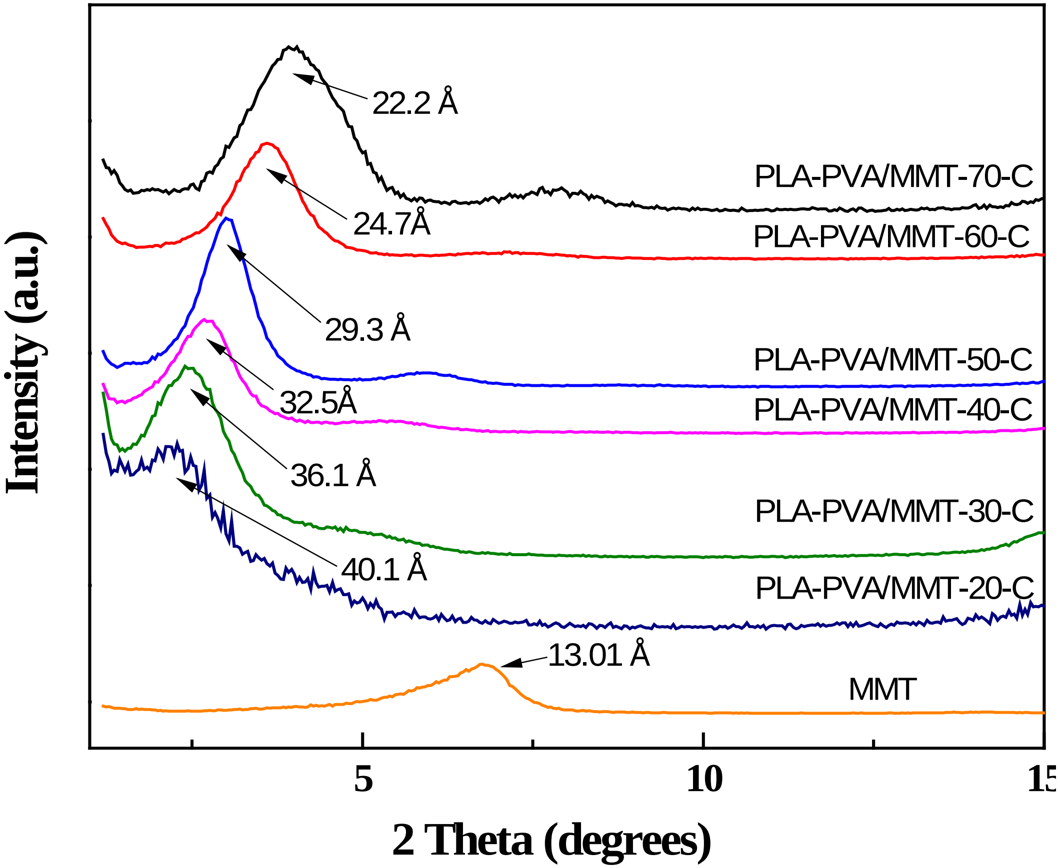
- **Property**
  - Superior mechanical properties (stiffer, anti-scratchability)
  - High barrier properties (to water vapor, oxygen, etc.)
  - Flame retardancy
  - High transparency
  - Other properties (printability, …)

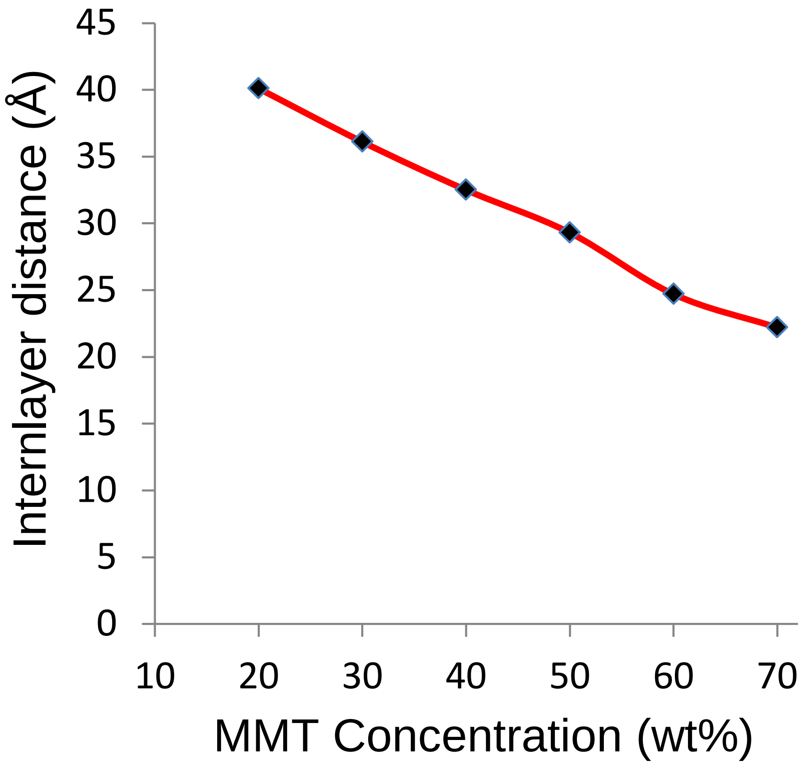
- **Applications**
  - Versatile (applicable to various substrates and surfaces)
    - Flat and curved; regular and irregular
    - Films, laminates, and rigid containers, etc.
  - Packaging, auto, construction, etc.

Digital Pictures and UV-Vis Spectra of Coated Films



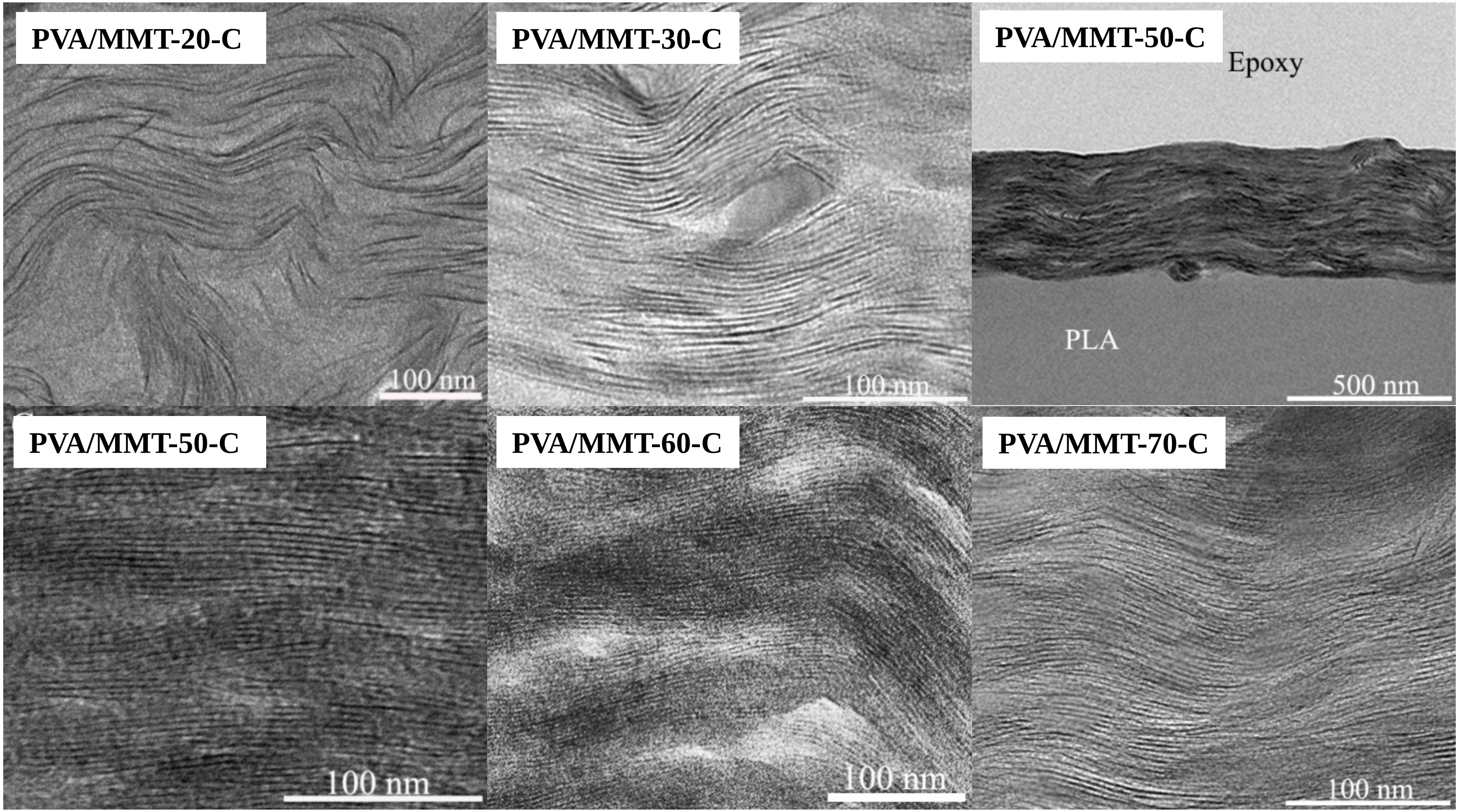
XRD Patterns of Coassembled PVA/MMT Nanocoatings on PLA Films

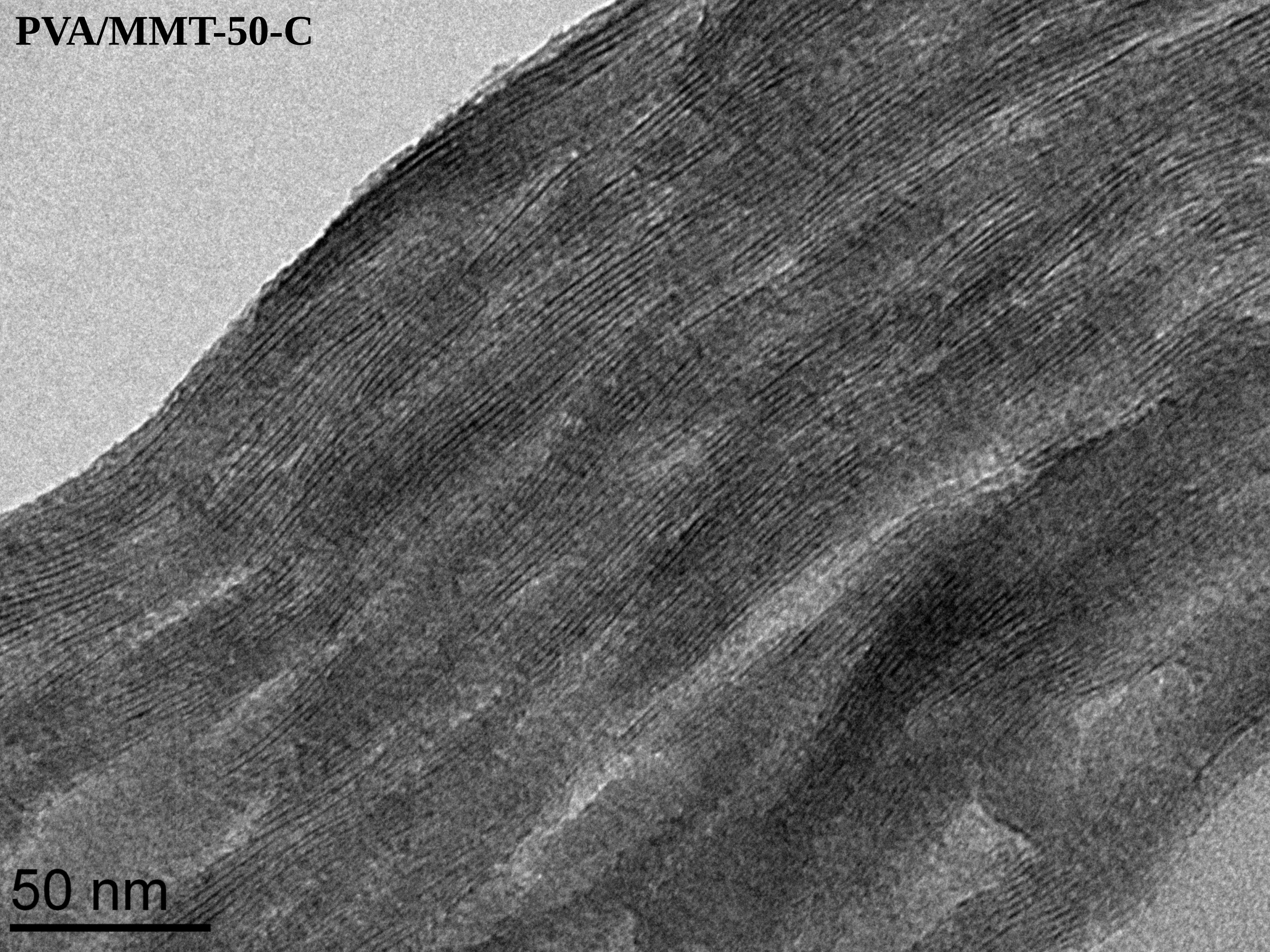




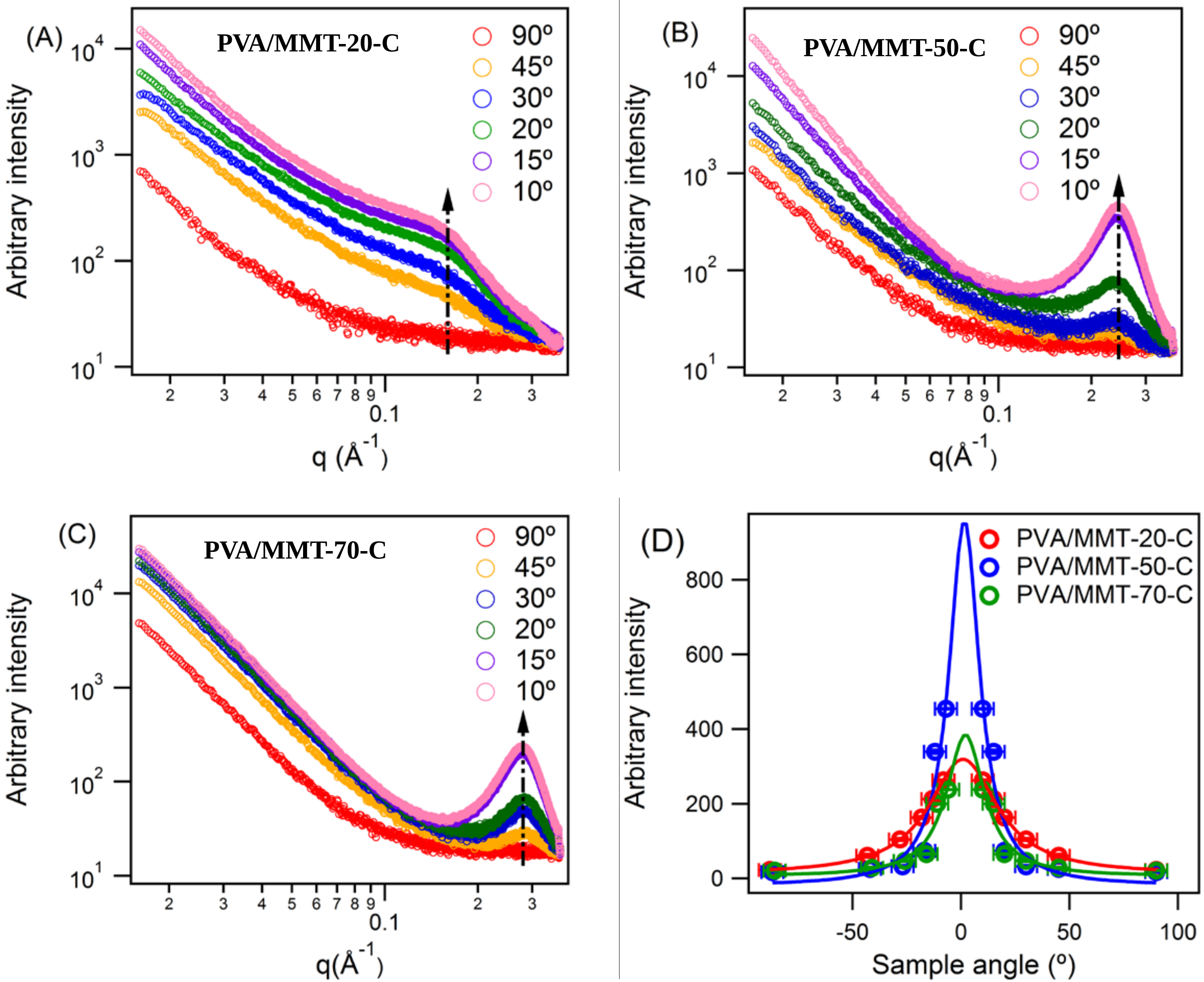
TEM Images of the Cross-section of Coassembled Nanocoatings

PVA/MMT-30-C

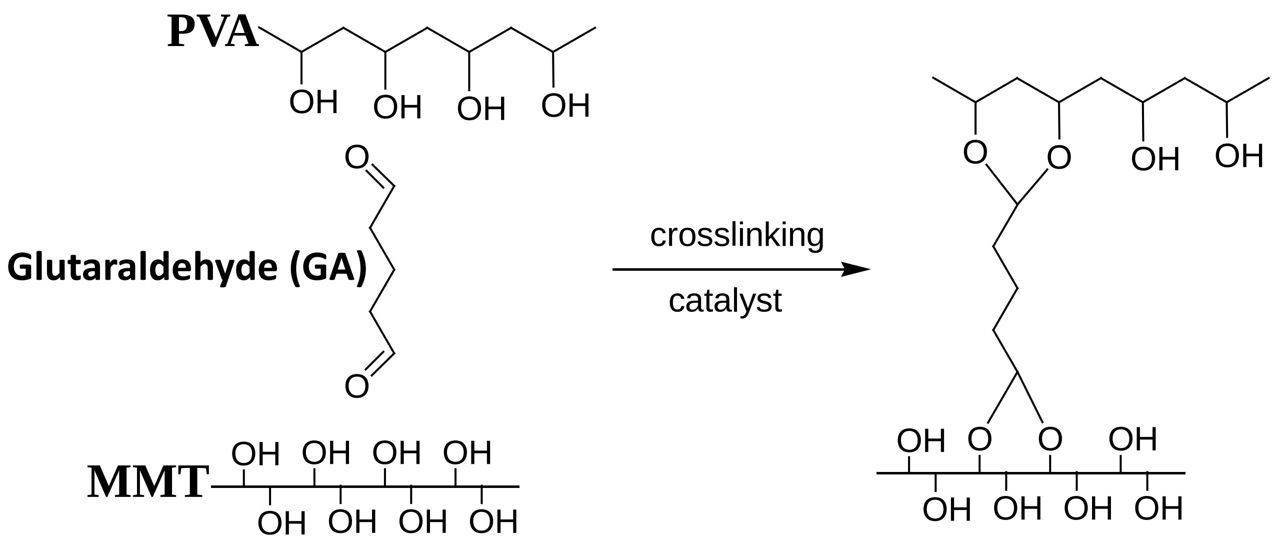


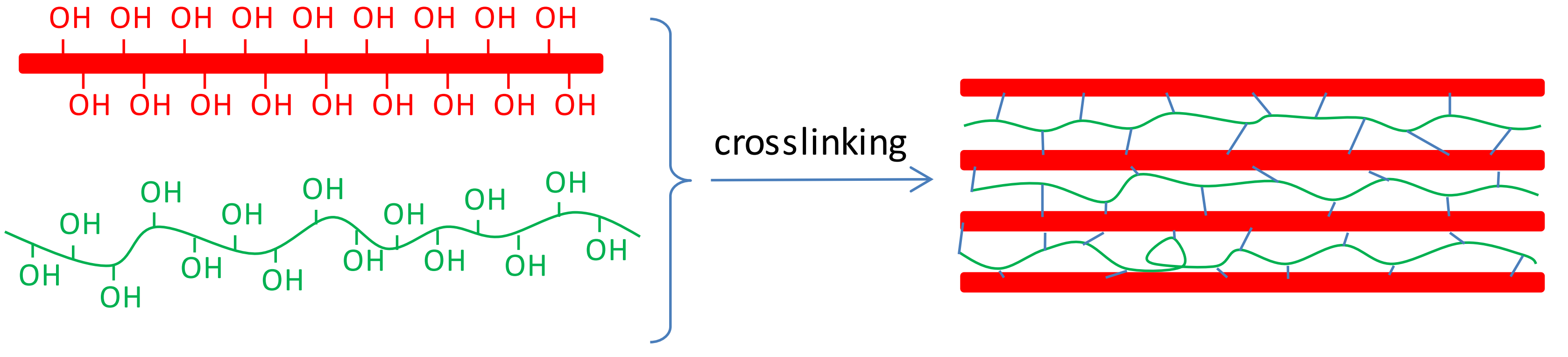

PVA/MMT-50-C
50 nm

Small Angel X-ray Scattering Characterization of Nanocoatings



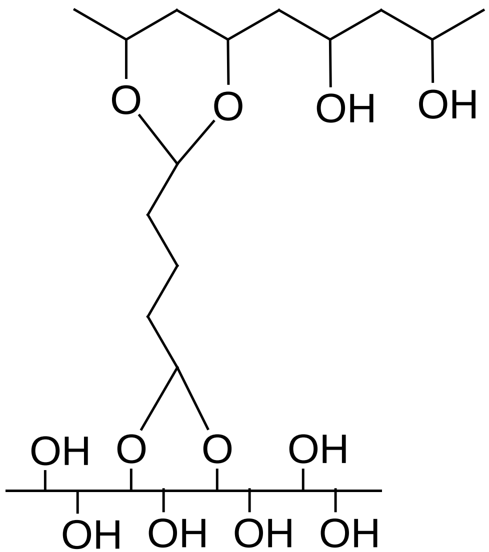
Integration of Aligned MMT/ZrP Nanosheets into PVA Matrix: Co-crosslinking

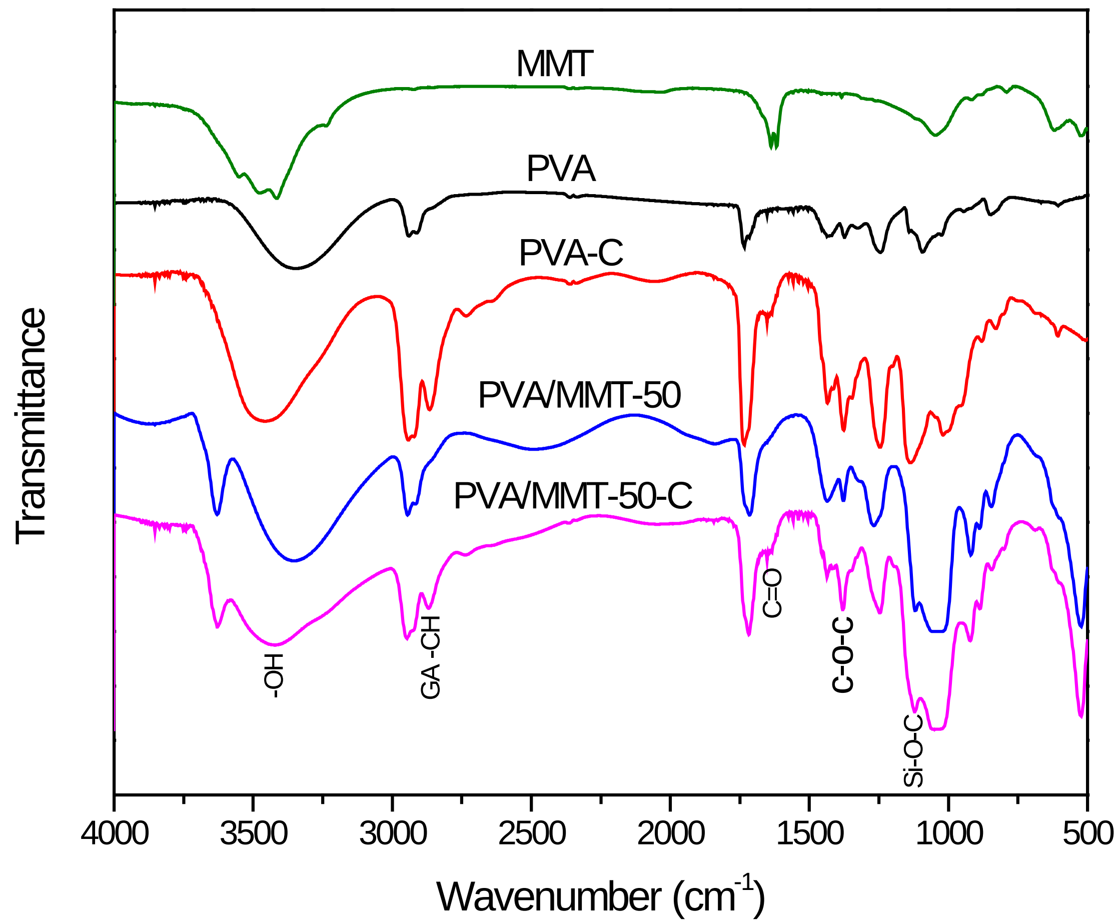




Many others nanosheets (such as α-zirconium phosphate) containing hydroxyl groups can be similarly co-crosslinked

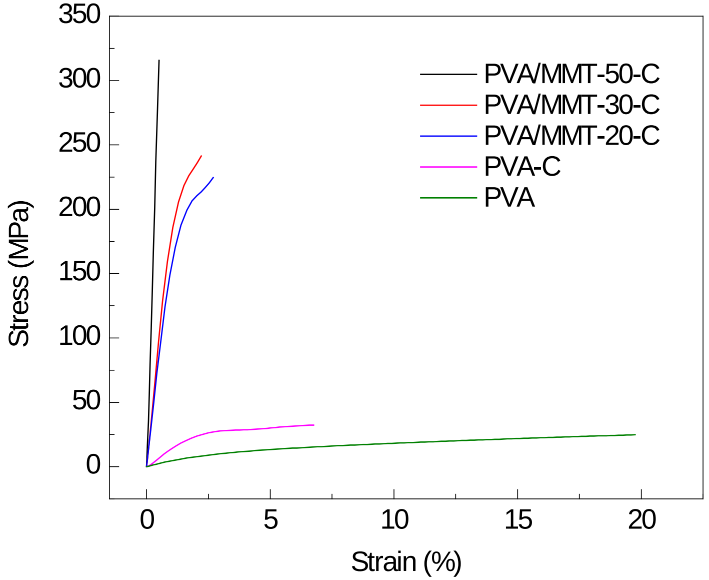
FTIR Spectra: Proof of Crosslinking

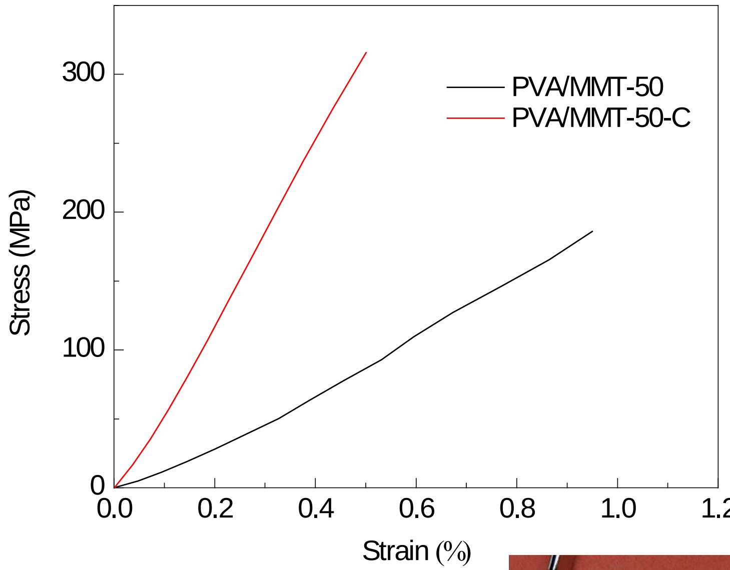




Crosslinked nanocoating does not dissolve in water

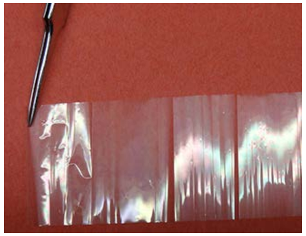
Mechanical Properties of Nanocoatings





Sample	Tensile strength (MPa)	Young's modulus (GPa)	Strain (%)	Density (g/cm³)	Specific strength (MPa·cm³/g)	Specific modulus (GPa·cm³/g)
PVA	24.8 ± 2.2	0.5 ± 0.1	19.8 ± 2.3	-	-	-
PVA-C	32.3 ± 2.6	1.5 ± 0.2	6.7 ± 0.8	-	-	-
PVA/MMT-20-C	224.6 ± 18.6	16.8 ± 2.1	2.7 ± 0.5	1.43	158	11.8
PVA/MMT-30-C	241.4 ± 24.1	20.0 ± 2.8	2.2 ± 0.3	1.52	159	13.2
PVA/MMT-50-N	185.9 ± 20.6	20.0 ± 2.5	1.0 ± 0.2	1.75	106	11.5
PVA/MMT-50-C	**315.7 ± 28.2**	**65.0 ± 4.8**	0.5 ± 0.1	1.75	**181**	**37.2**
Nacre	80-135	60-70	0.2-0.9	2.65	30.2-50.9	22.6-26.4
Aluminum alloy 2014 (annealed)	185	70	-	2.73	67.8	26
Stainless steel type 304	550	195	-	7.90	69.6	25

**CRC Handbook of Chemistry and Physics*, 90th ed.

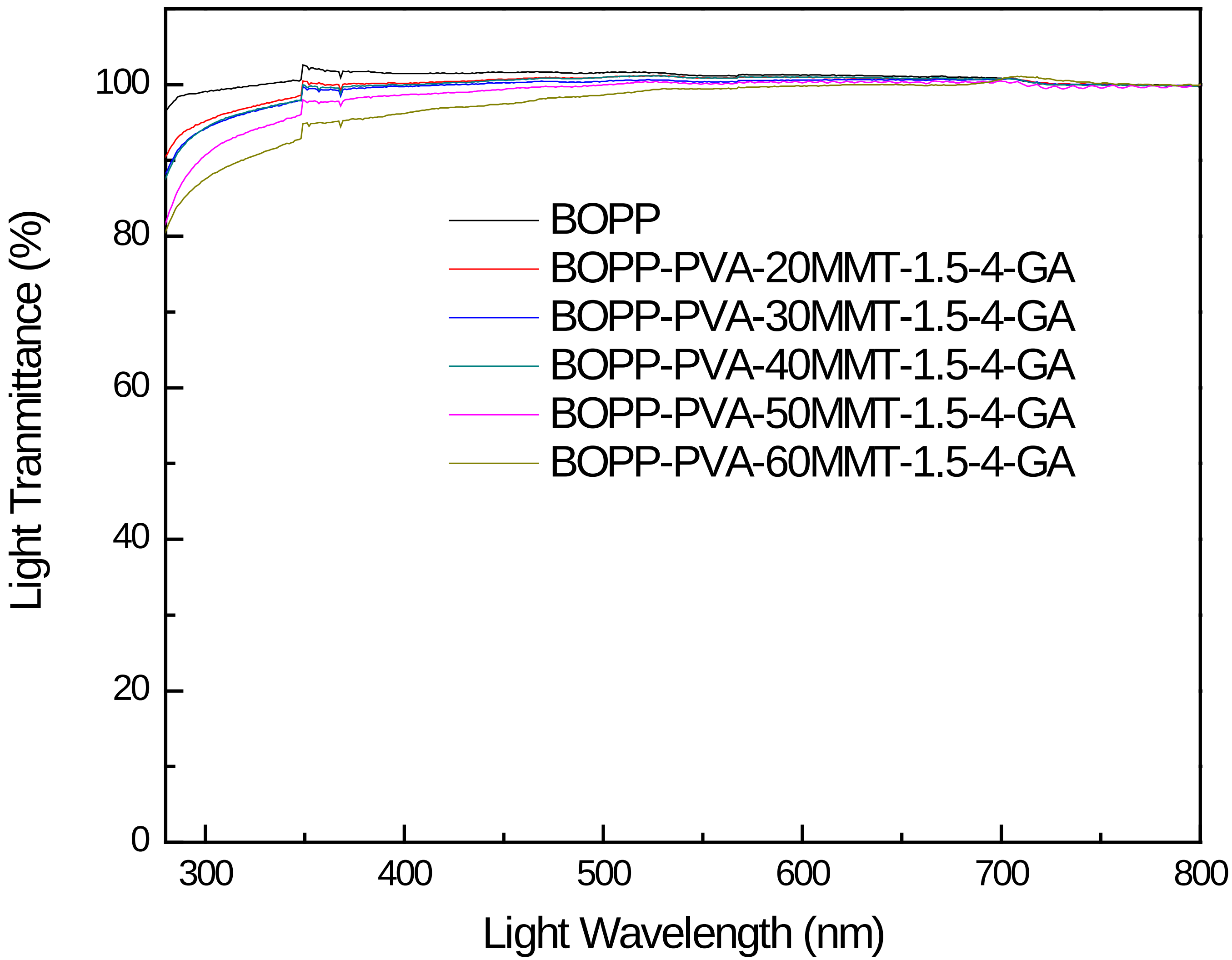


OTR and WVTR of Coated Films

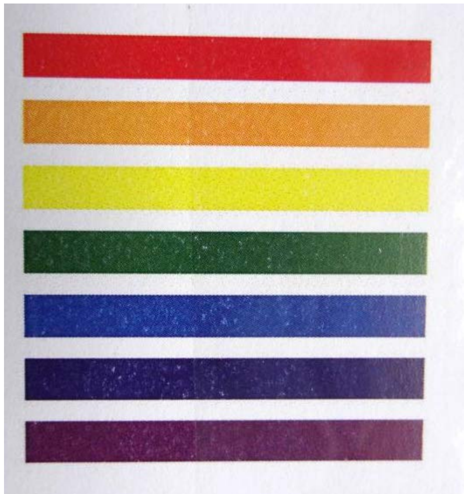
Formulation in graft	Nanocoating thickness (nm)	Number of clay layers	WVTR [g/(m²•day)]	OTR [mL/(m²•day)]	O_2 Permeability of coated film [10^{-16}cm³(STP) •cm/cm²•s•Pa]	O_2 Permeability of coating layer [10^{-16}cm³(STP) •cm/cm²•s•Pa]	BIF
PLA (20 µm)	-	-	98.2	1205.0	275.29	-	-
PLA-PVA	450 ± 25	-	34.8	9.4	2.20	0.0488	125
PLA-PVA-C	510 ± 26	-	31.4	7.4	1.73	0.0433	159
PLA-PVA/MMT-20-C	560 ± 34	140 ± 8	26.4	3.6	0.85	0.0232	324
PLA-PVA/MMT-30-C	600 ± 30	166 ± 8	18.9	1.5	0.35	0.0102	787
PLA-PVA/MMT-40-C	608 ± 24	187 ± 7	14.5	0.6	0.14	0.0041	1966
PLA-PVA/MMT-50	590 ± 32	220 ± 12	17.2	0.2	0.05	0.0014	5506
PLA-PVA/MMT-50-C	620 ± 23	212 ± 8	13.1	0.2	0.05	0.0015	5506
PLA-PVA/MMT-60	610 ± 24	260 ± 10	15.6	0.2	0.05	0.0015	5506
PLA-PVA/MMT-60-C	620 ± 31	251 ± 13	10.9	0.2	0.05	0.0015	5506
PLA-PVA/MMT-70-C	650 ± 25	293 ± 11	10.1	0.1	0.02	0.0006	13765
PET (24 µm)	-	-	4.1	64.0	16.08	-	-
PET-PVA-C	596 ± 29	-	3.1	14.8	3.82	0.1311	4
PET-PVA/MMT-50-C	625 ± 20	213 ± 7	2.6	0.1	0.03	0.0008	585
BOPP (20 µm)	-	-	1.1	1860.0	424.93	-	-
BOPP-PVA-C	570 ± 30	-	0.4	45.0	10.57	0.3002	40
BOPP-PVA/MMT-50-C	615 ± 25	210 ± 8	0.6	0.2	0.05	0.0015	8499
HDPE (25.4 µm)	-	-	0.6	2530.0	734.05		-
HDPE-PVA-C	625 ± 33	-	0.4	33.0	9.81	0.2387	75
HDPE-PVA/MMT-50-C	680 ± 26	239 ± 9	0.5	0.4	0.12	0.0031	6117
LDPE (25.4 µm)	-	-	2.1	4050.0	1175.06	-	-
LDPE-PVA-C	600 ± 28	-	1.7	40.8	12.12	0.2825	97
LDPE-PVA/MMT-50-C	625 ± 22	213 ± 7	1.3	0.1	0.03	0.0007	39169

Oxygen transmission rates (OTRs) were tested on a MOCON OX-TRAN 1/50 OTR tester (ASTM D-3985) at 23 °C and 0% RH. Water vapor transmission rates (WVTRs) were tested on a MOCON PERMATRAN-W 1/50 WVTR tester (ASTM F-1249) at 23 °C and 50% RH.

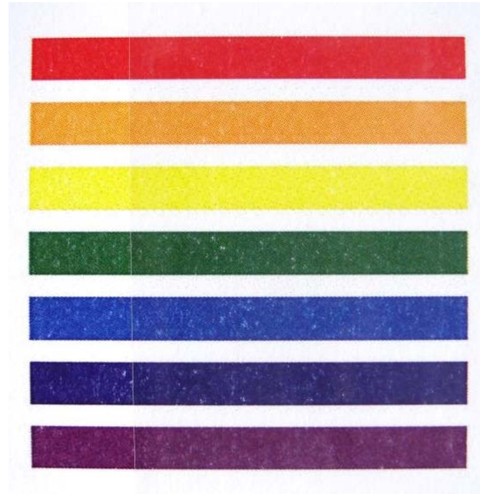
Nanocoating on BOPP Films



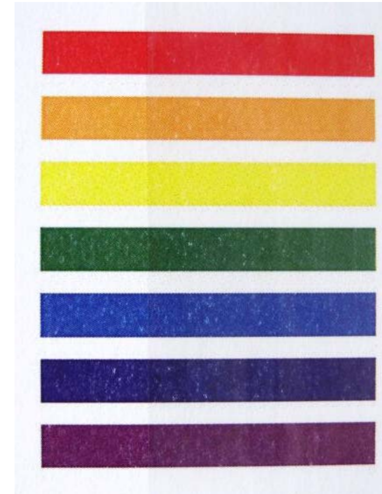
Transparency of Coated BOPP Films



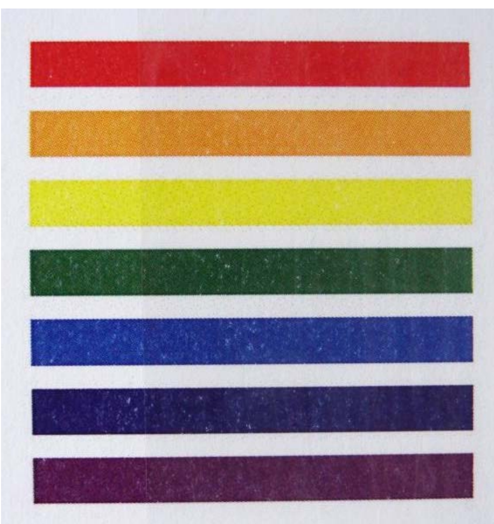
BOPP



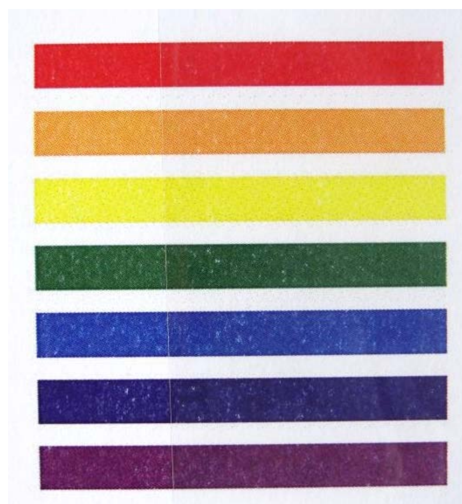
BOPP-PVA-60MMT-1.5-4-GA



BOPP-PVA-50MMT-1.5-4-GA



BOPP-PVA-40MMT-1.5-4-GA

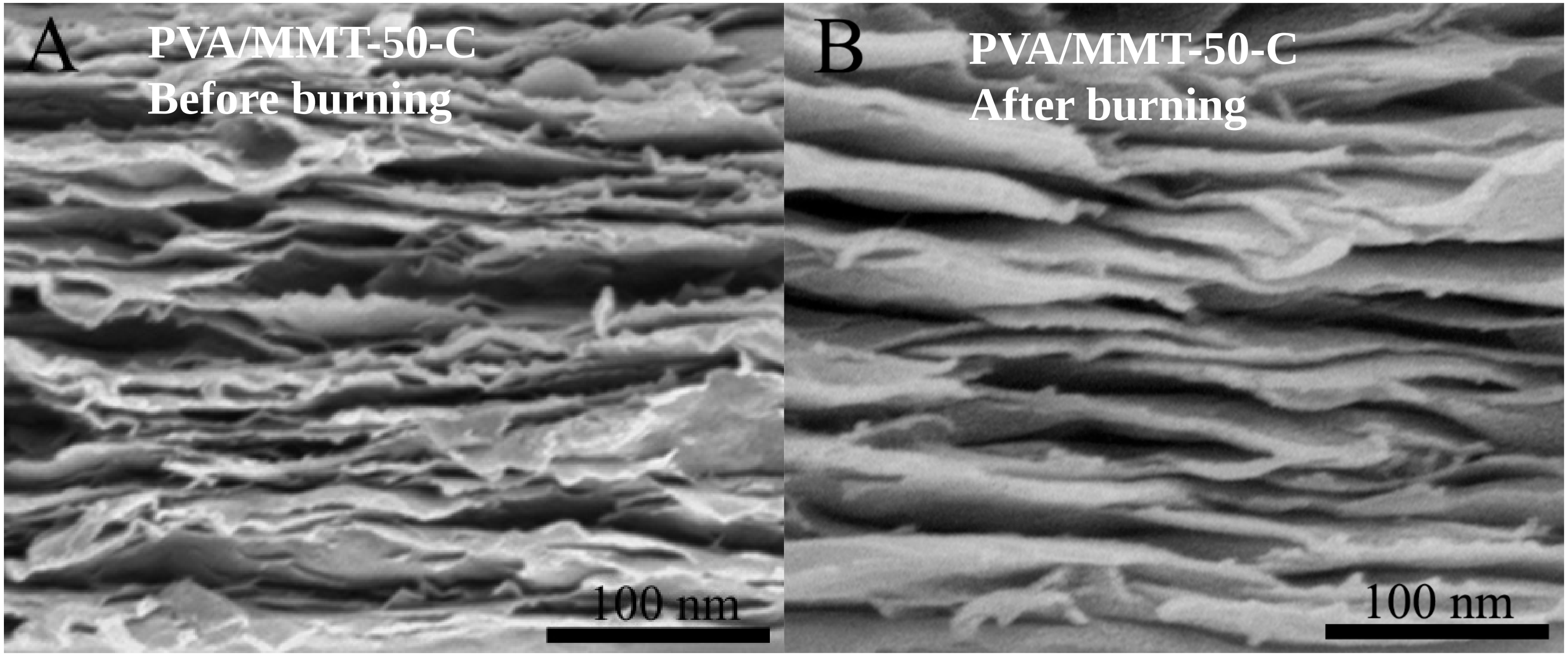


BOPP-PVA-30MMT-1.5-4-GA

BOPP-PVA-20MMT-1.5-4-GA

Brief Flame Retardancy Evaluation

Morphology Before and After Ignition Test



Nanocoatings from Coassembly of Polymers and Inorganic Nanosheets --- Achieved

- **Property**
  - Superior mechanical properties (stiffer, anti-scratchability)
    - ca. 1/3 stiffness of stainless steel, and 2/3 strength of stainless steel
  - High barrier properties (to water vapor, oxygen, etc.)
    - Oxygen barrier comparable to the metalized films (for chip packaging)
  - Flame retardancy
  - High transparency
  - Other properties (printability, …)
- **Applications**
  - Versatile (applicable to various substrates and surfaces)
    - Flat and curved; regular and irregular
    - Films, laminates, and rigid containers, etc.
  - Packaging, auto, construction, etc.

Summary

- High loading; high orientation; complete integration
- Superior oxygen barrier and flame retardancy, outstanding mechanical properties
- Overcome the conflict between high level of dispersion and viscosity
- Overcome the conflict between high performance and cost
  - Achieved high loading but a very thin film (ca. 300 nm)
- A facile process viable for commercialization