

Effect of UV Exposure on Surface and Interface Properties of PMMA-co-PEA/PVDF Blends

Project #3

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Results: AFM and FTIR-ATR

- PMMA-co-PEA/PVDF Blends: 70/30, 50/50, 30/70
- Surface and Interface

Exposure Conditions:

UV source: 1000 W Xenon arc lamp

Temperature: 50 °C

Relative humidity: ~ 9%

Exposure Duration: 7 months

AFM Phase Imaging (Tapping Mode)

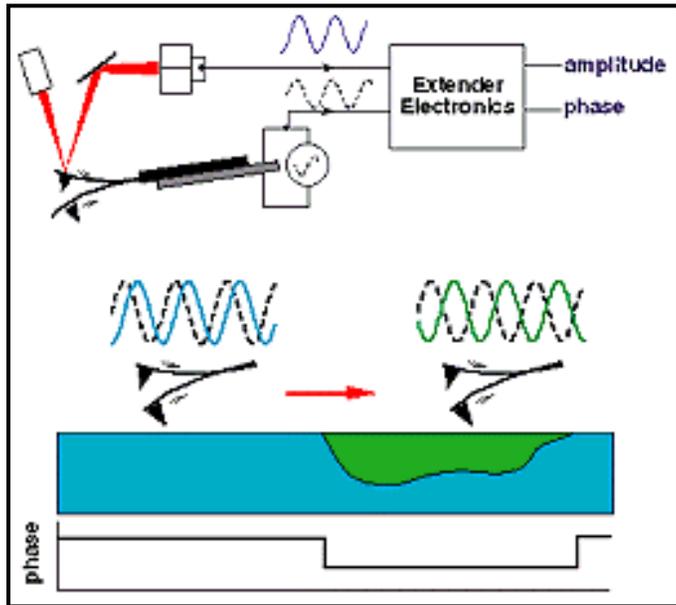
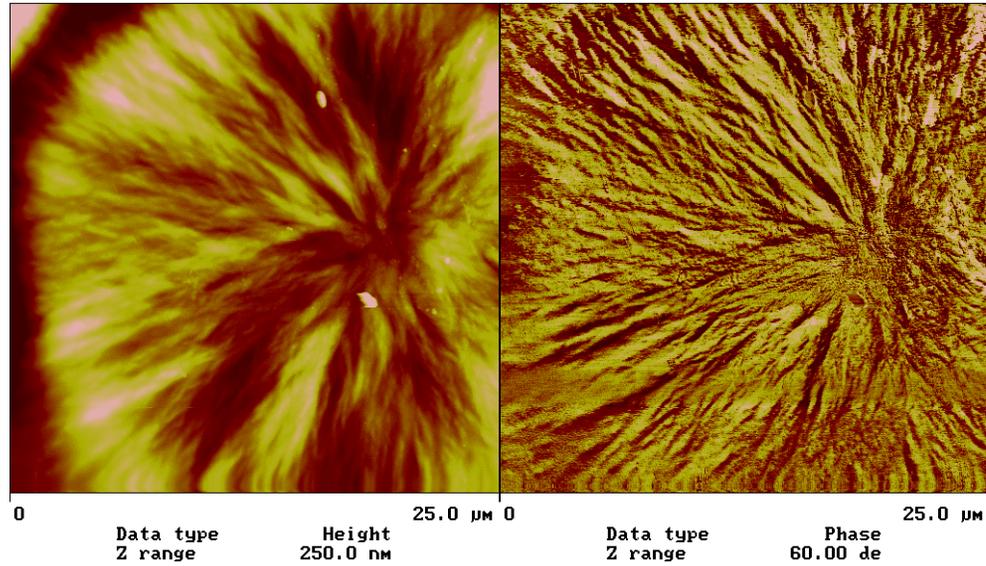


Illustration courtesy of Digital Instruments

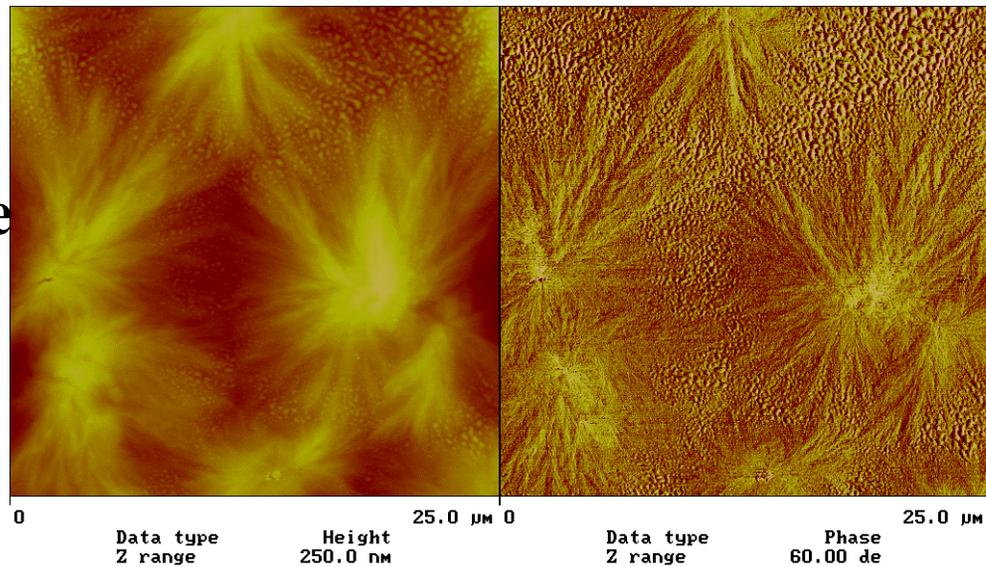
- The cantilever probe is oscillated at its resonance frequency such that it makes contact (taps) with the sample only for a short duration in each oscillation cycle.
- As the tip approaches the sample, the tip-sample interactions change the amplitude, the resonance frequency, and the phase angle of the oscillating probe.
- Monitoring the amplitude of the oscillation provides topographic images.
- Monitoring changes in the phase of the oscillating probe can often provide useful information on the properties of the imaged areas.
- “What sample properties affect phase images” still remains an unanswered question.

PMMA-CO-PEA/PVDF: 30/70 (by Mass)

Film/Air Interface

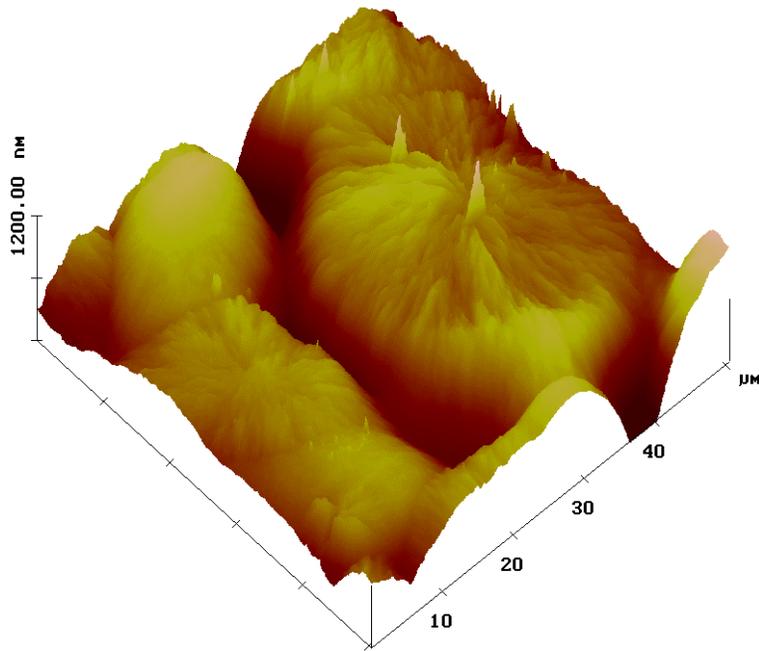


Film/Glass Interface

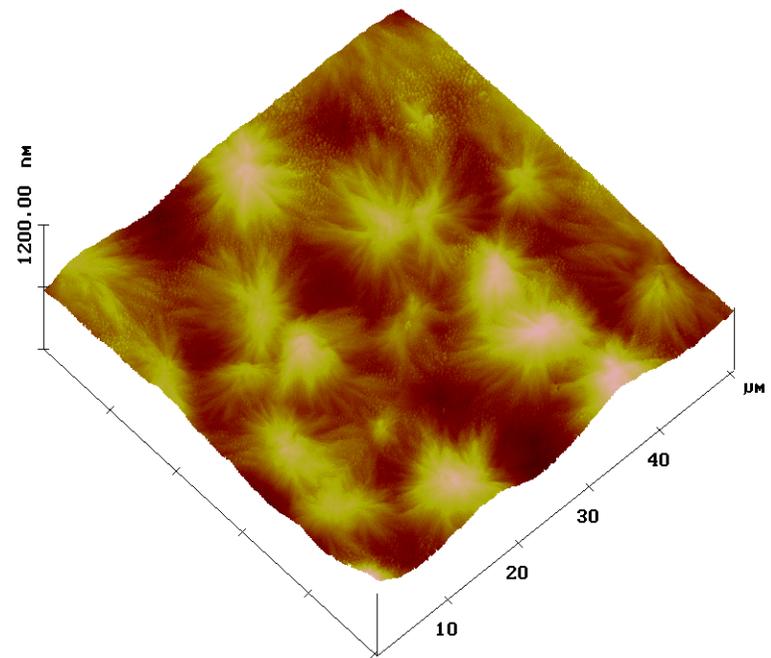


PMMA-CO-PEA/PVDF: 30/70 (by Mass)

Film/Air Interface



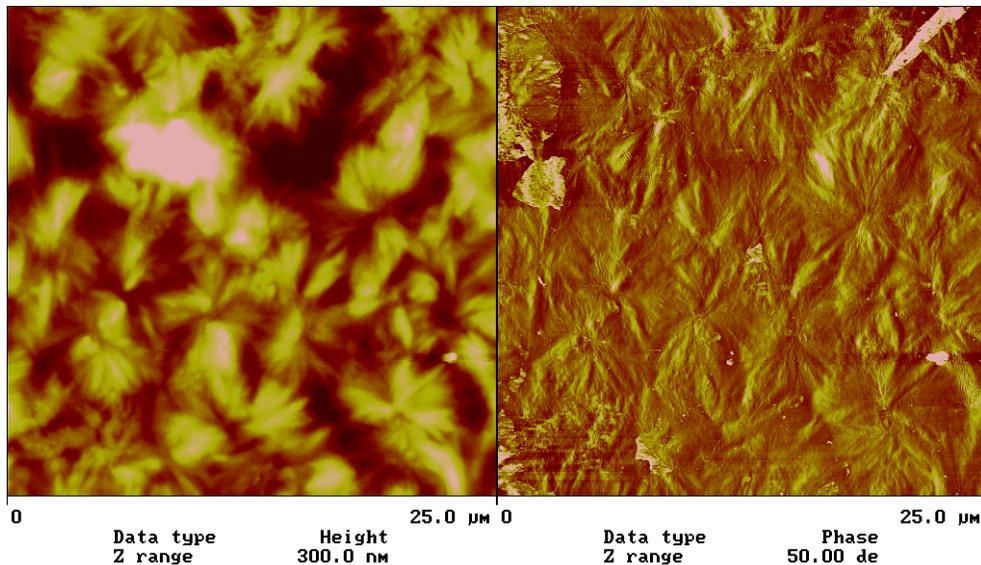
Film/Glass Interface



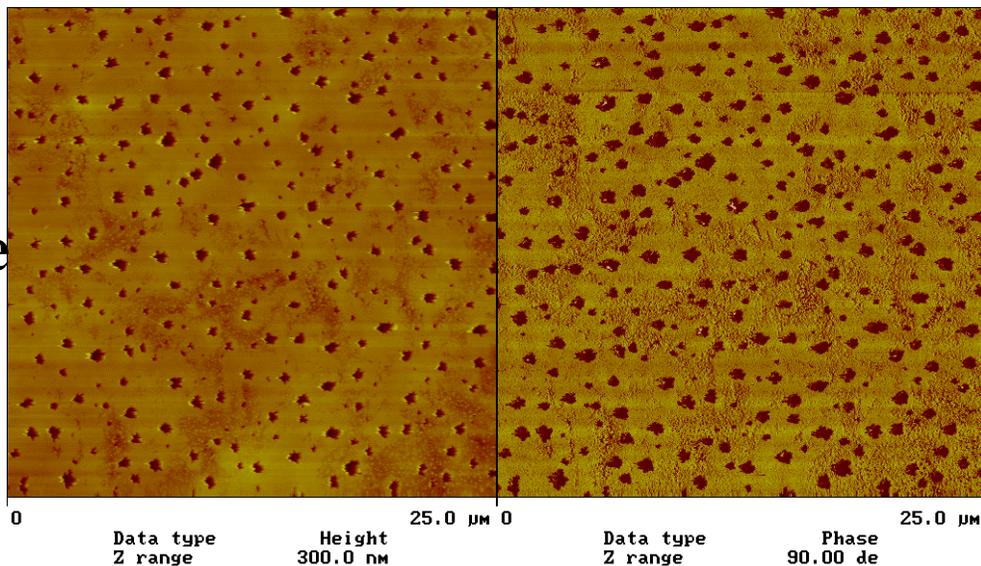
3-D

PMMA-CO-PEA/PVDF: 50/50 (by Mass)

Film/Air Interface



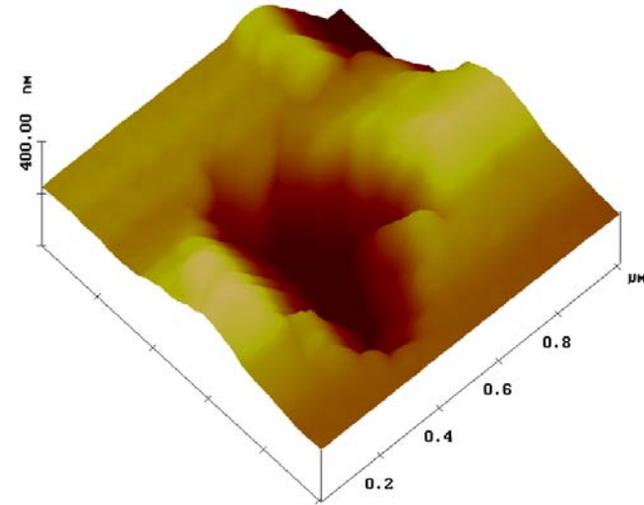
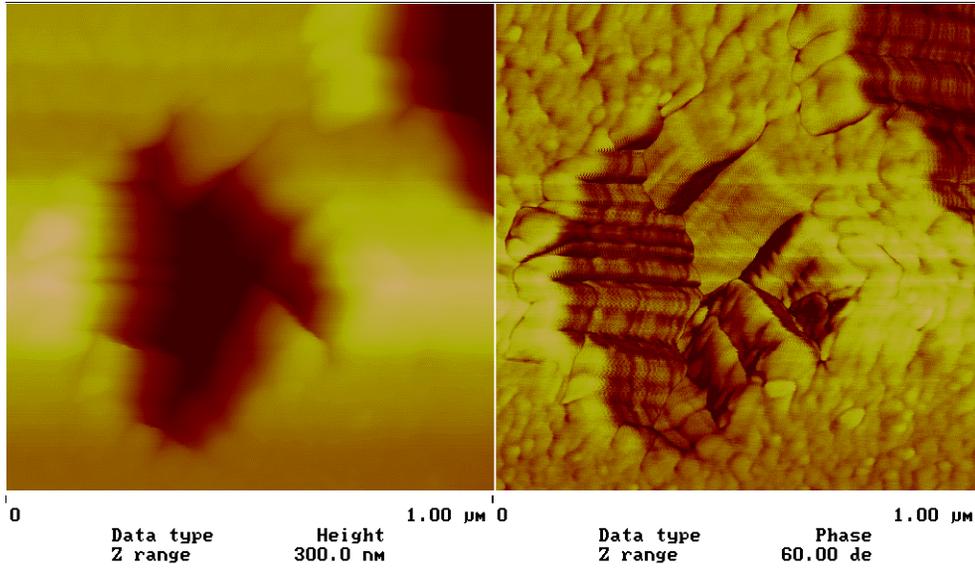
Film/Glass Interface



PMMA-CO-PEA/PVDF: 50/50 (by Mass)

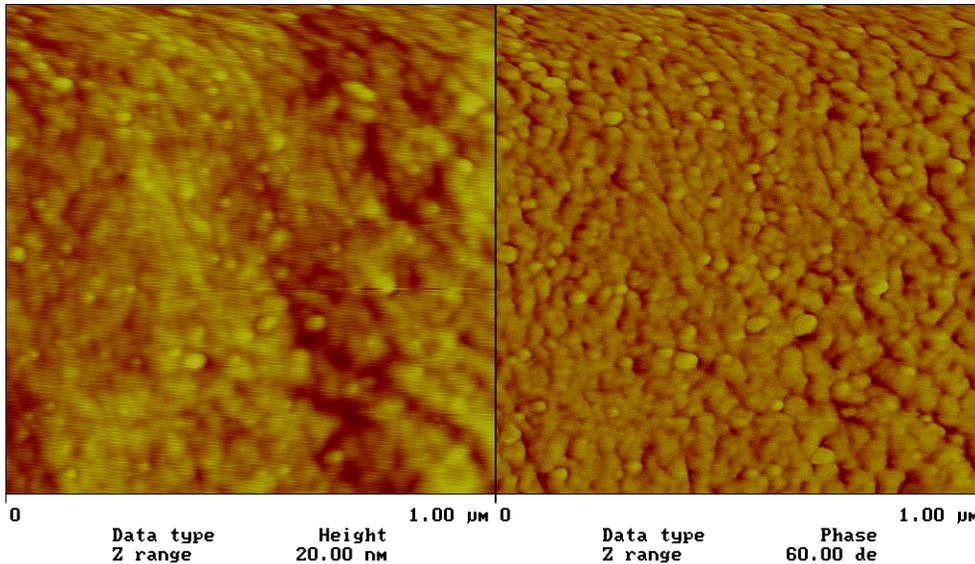
Film/Glass Interface

Hole



3-D of the Hole

Smooth Area

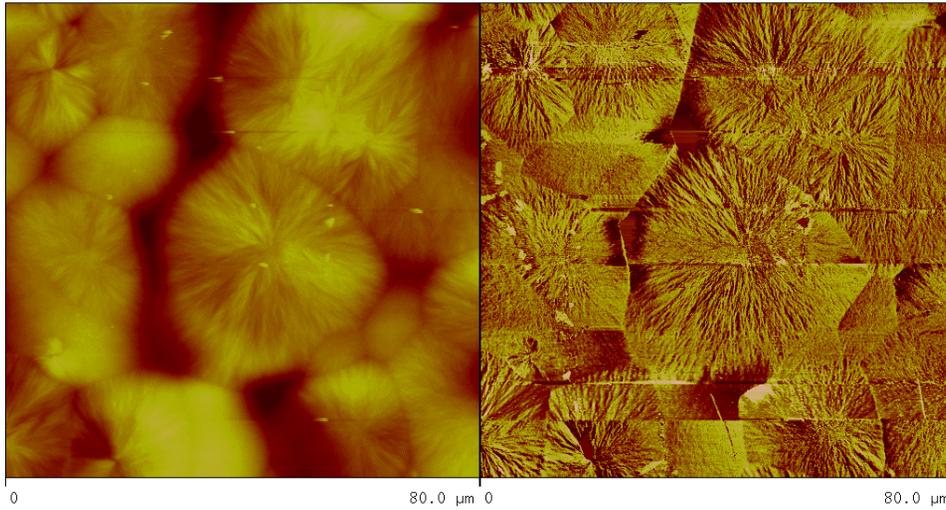


Wettability of Film/Air and Film/Substrate Interfaces of PVDF and Its Blends

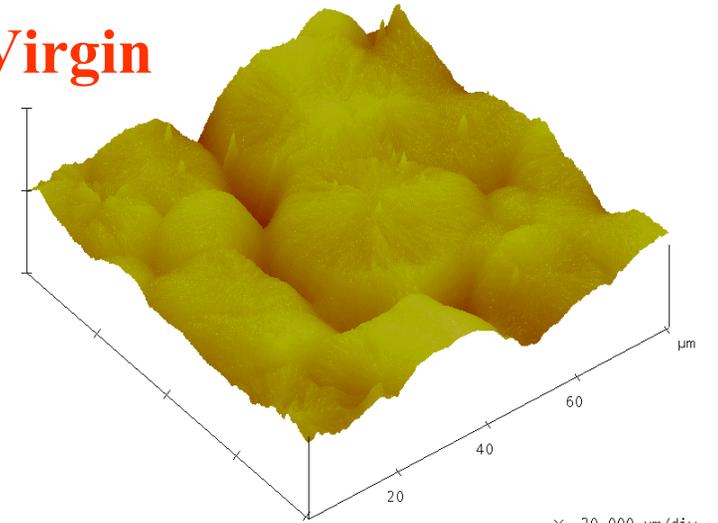
Sample	Side	γ^p , mJ/m ²	γ , mJ/m ²	x^p
PMMA-CO-PEA /PVDF, 70/30 m/m	Interface	21.8±0.7	44.3±0.5	0.49±0.02
	Surface	8.7±0.5	42.4±0.6	0.21±0.01
PMMA-CO-PEA /PVDF, 50/50 m/m	Interface	14.4±3.2	38.2±2.6	0.38±0.10
	Surface	7.7±1.9	43.2±1.4	0.18±0.05
PMMA-CO-PEA /PVDF, 30/70 m/m	Interface	13.4±1.3	45.9±1.1	0.29±0.03
	Surface	6.7±0.8	41.0±1.1	0.16±0.02

Surface free energy components were calculated using the geometric-mean method

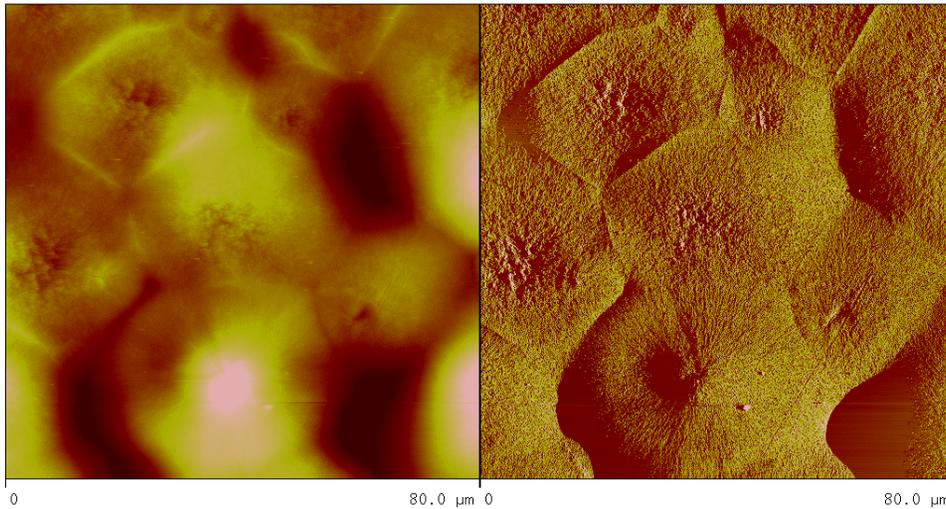
PMMA-CO-PEA/PVDF: 30/70; Surface



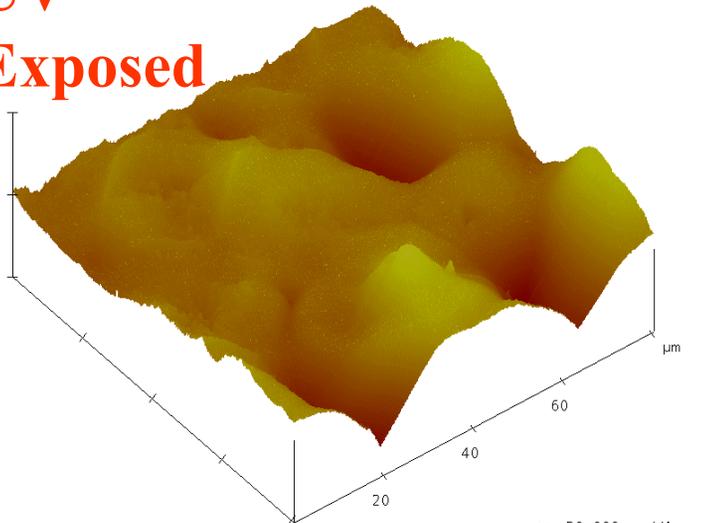
Virgin



X 20.000 μm/div
Z 1500.000 nm/div



UV Exposed



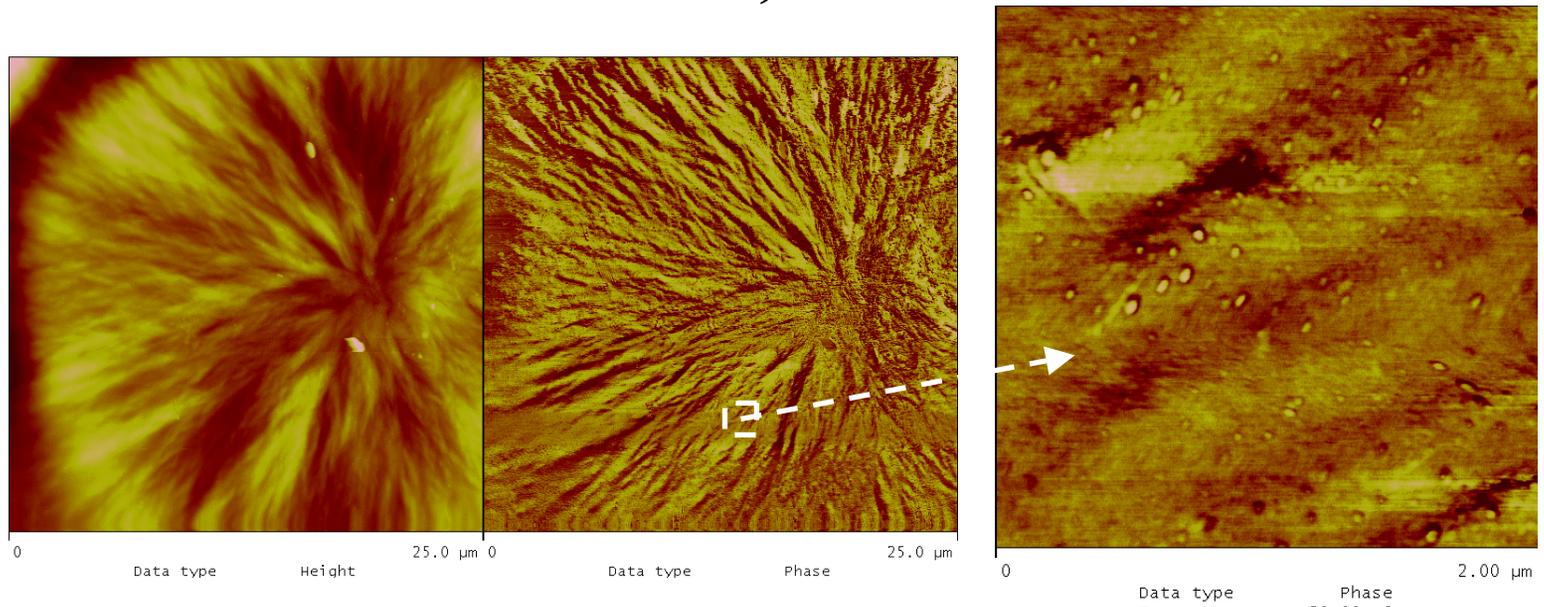
X 20.000 μm/div
Z 1500.000 nm/div

pf6.F02

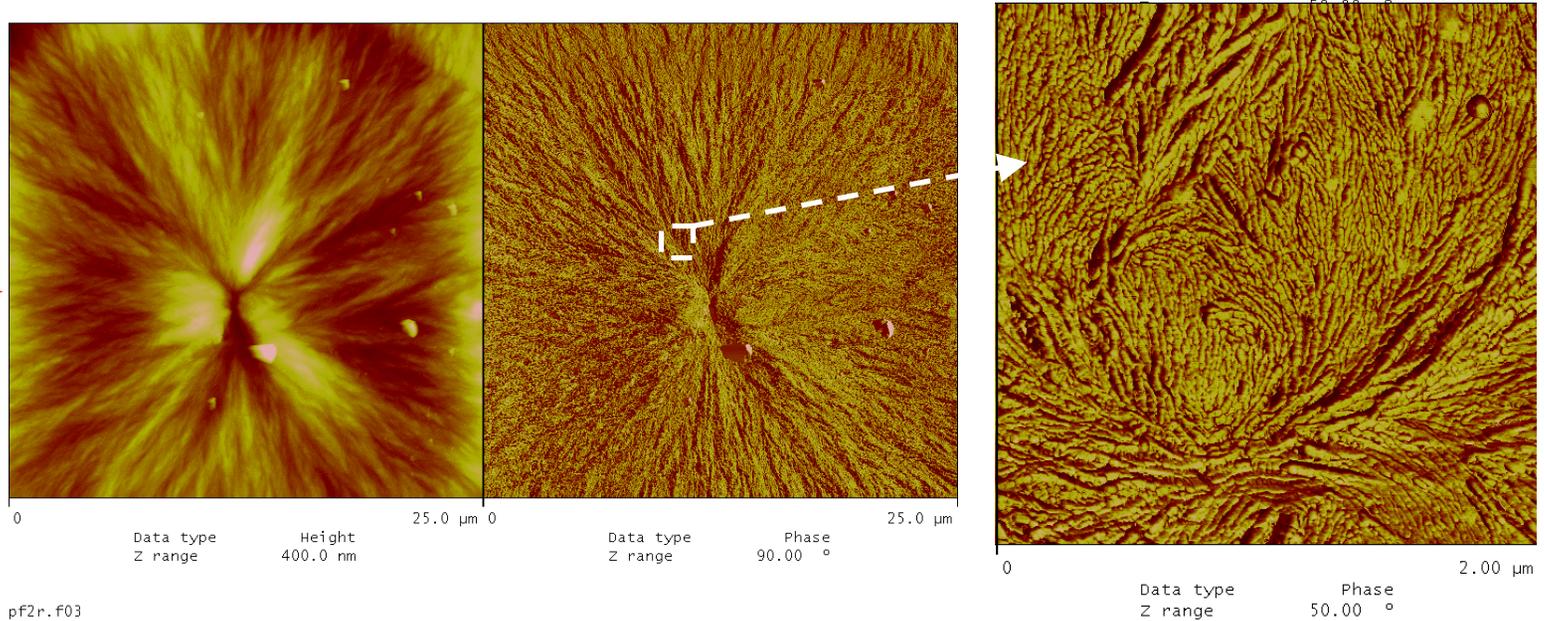
• Similar topography---PVDF crystals dominate the surface.

PMMA-CO-PEA/PVDF: 30/70; Surface

Virgin



UV Exposed

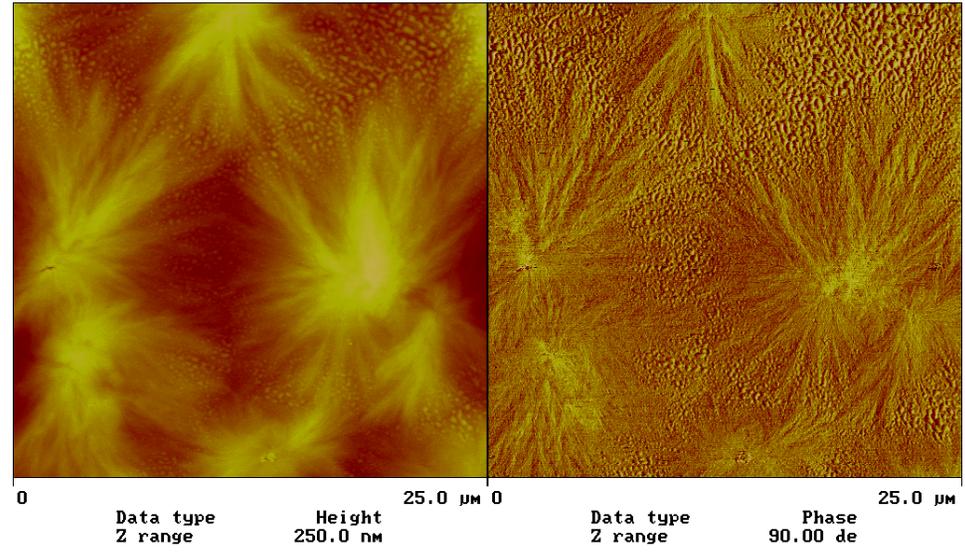
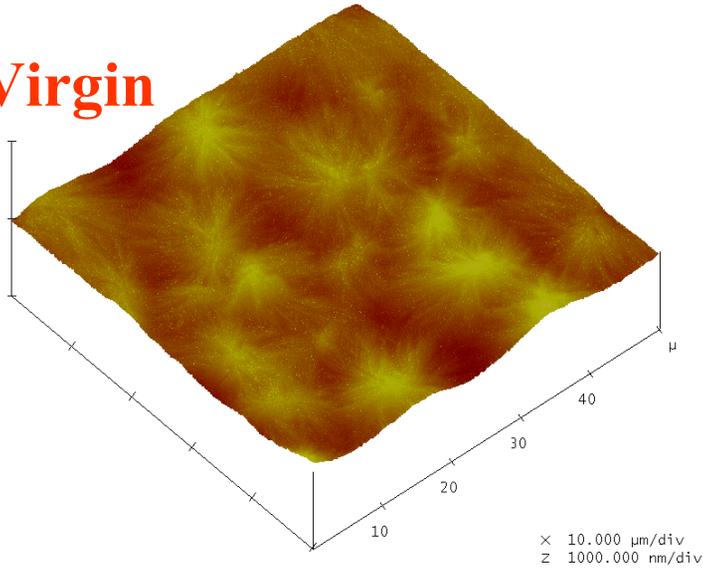


pf2r.f03

•Crystal structures become more organized.

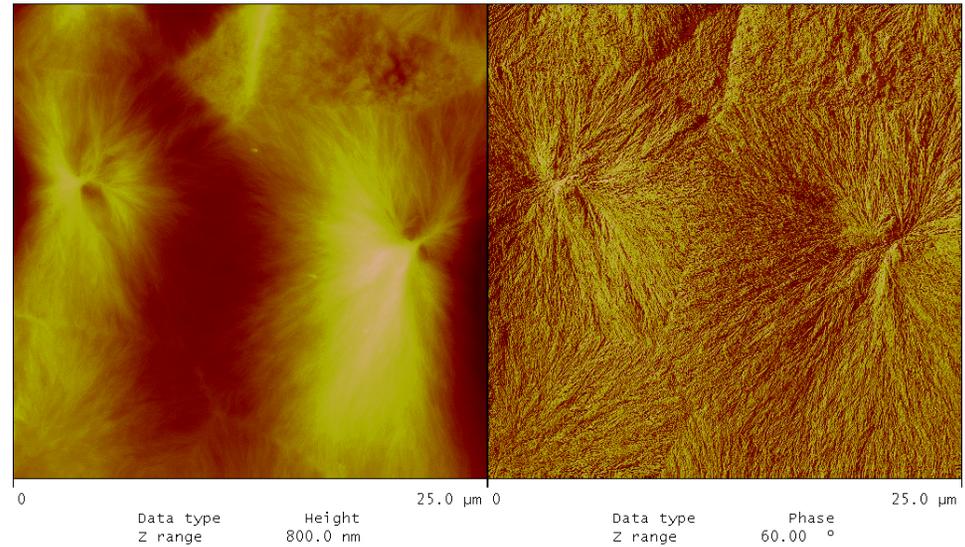
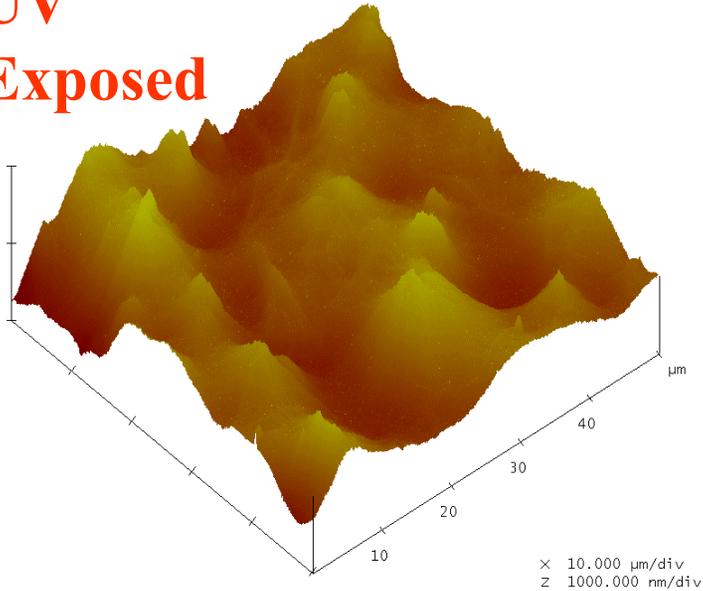
PMMA-CO-PEA/PVDF: 30/70; Interface

Virgin



3pm7pvq.f02

UV
Exposed

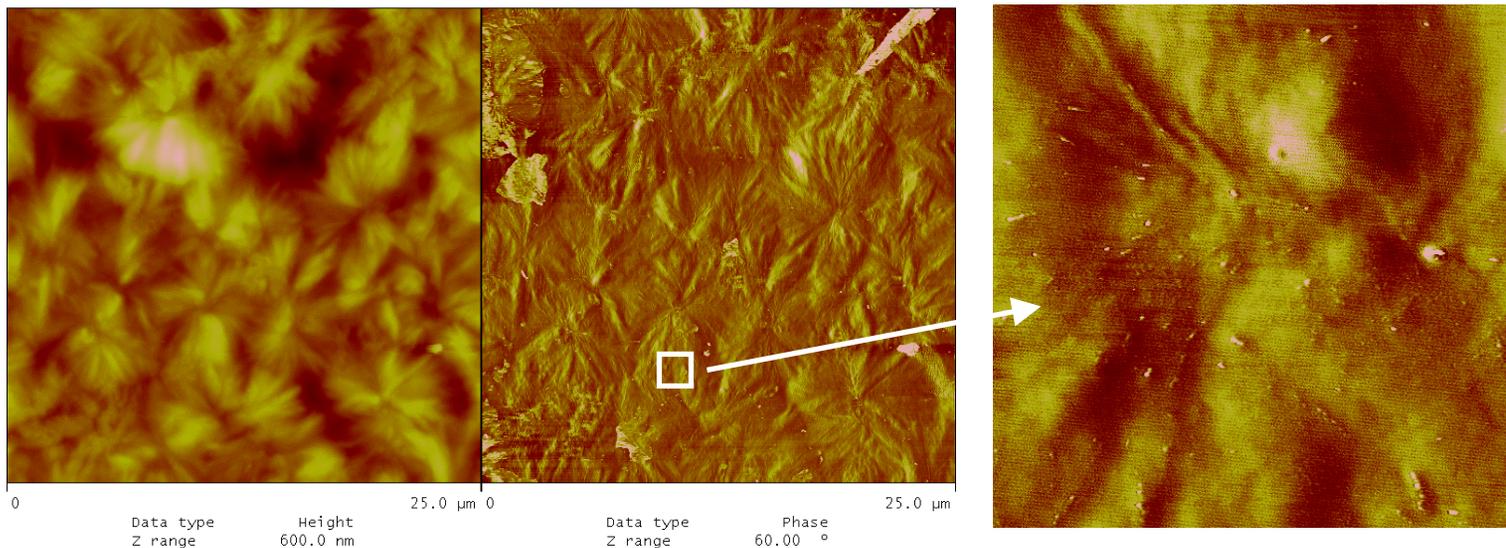


pf7.f03

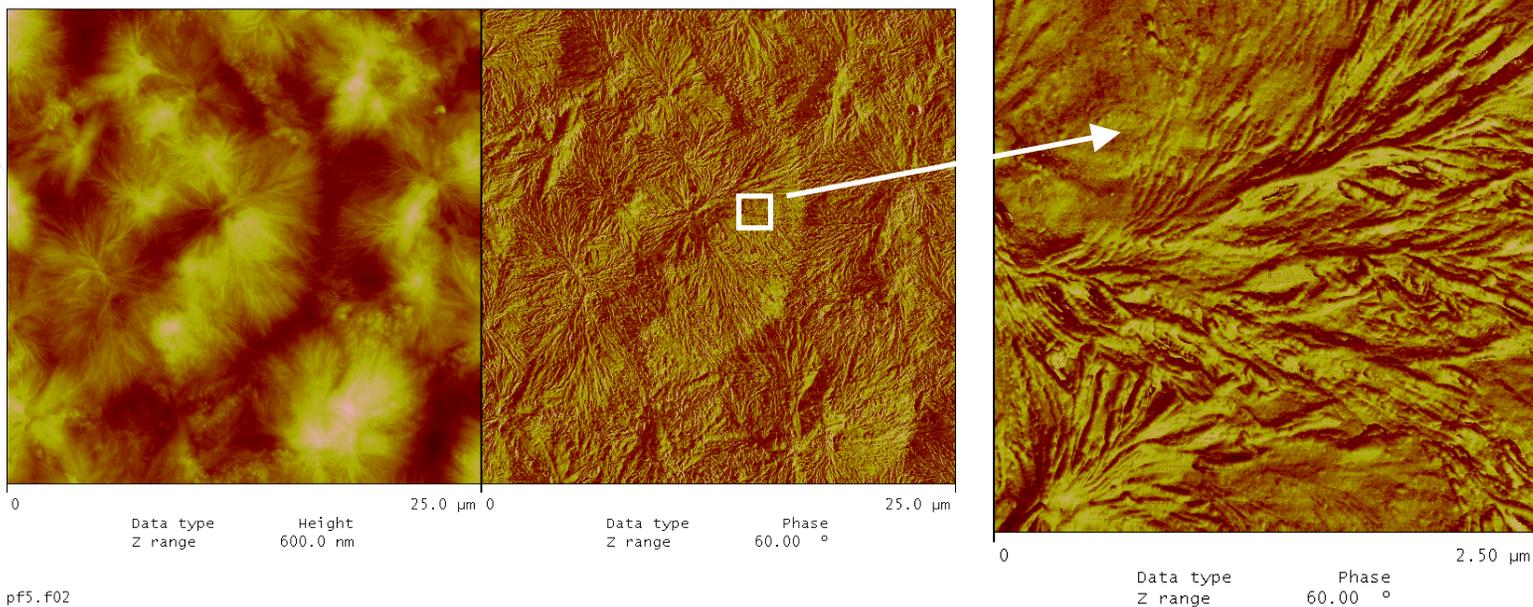
• Roughness is increased.

PMMA-CO-PEA/PVDF:50/50; Surface

Virgin



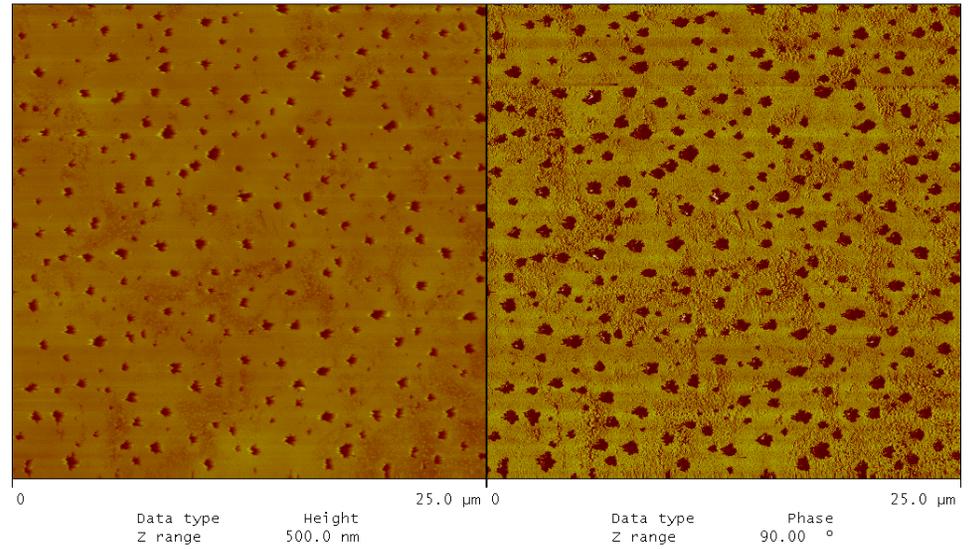
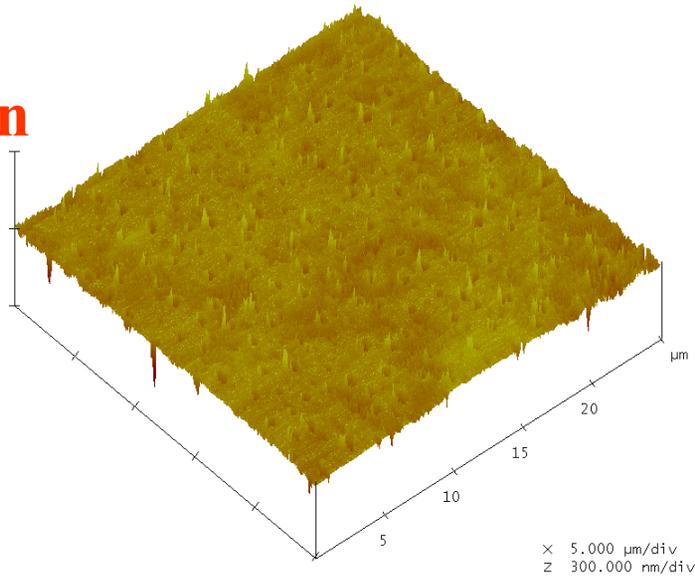
UV
Exposed



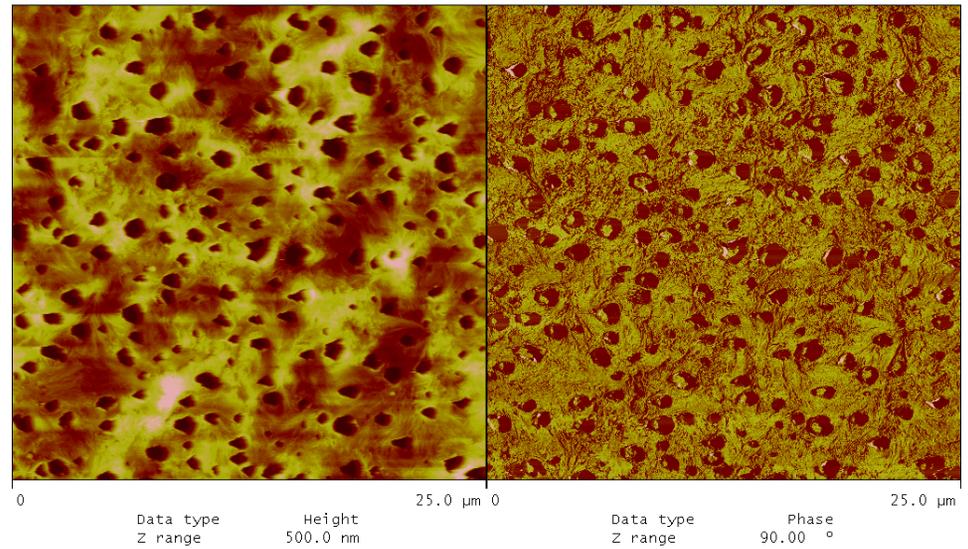
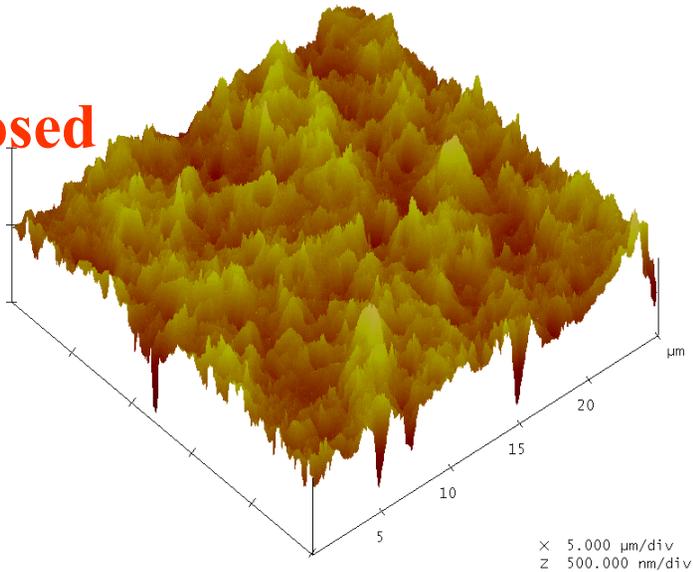
• More well-organized crystal structures are observed after UV exposure.

PMMA-CO-PEA/PVDF: 50/50; Interface

Virgin



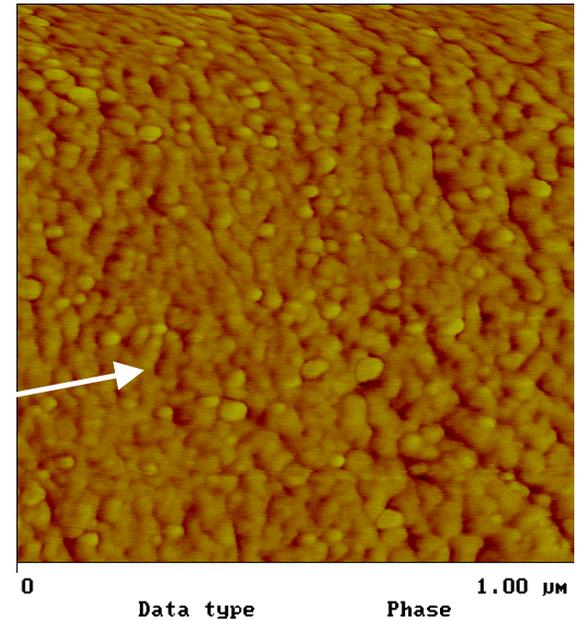
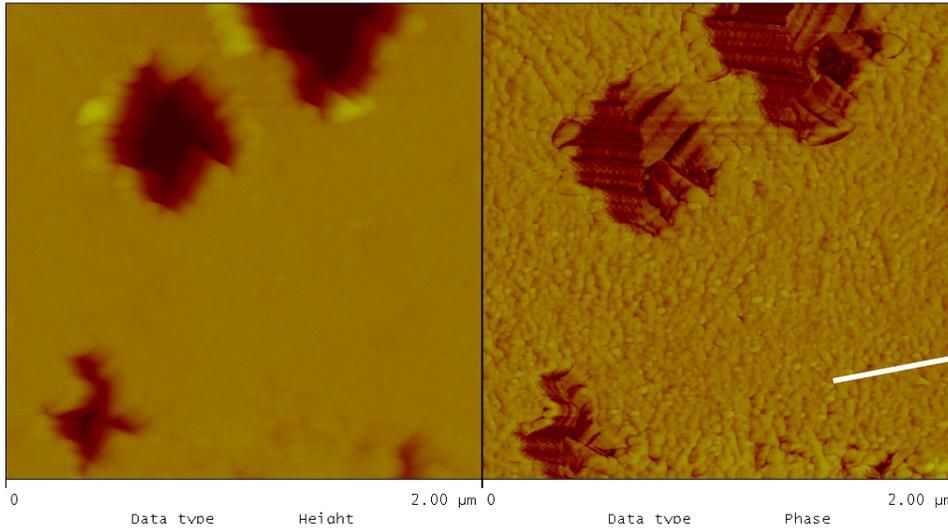
UV Exposed



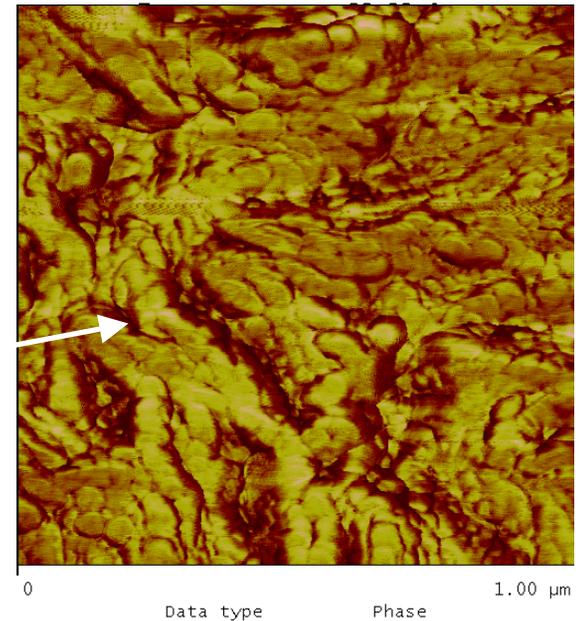
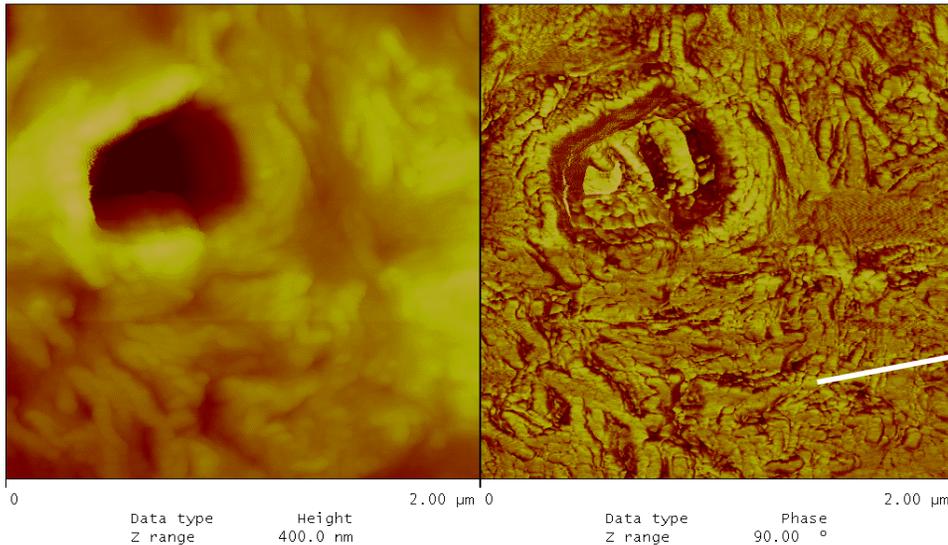
•Roughness is increased.

PMMA-CO-PEA/PVDF: 50/50; Interface

Virgin



UV Exposed

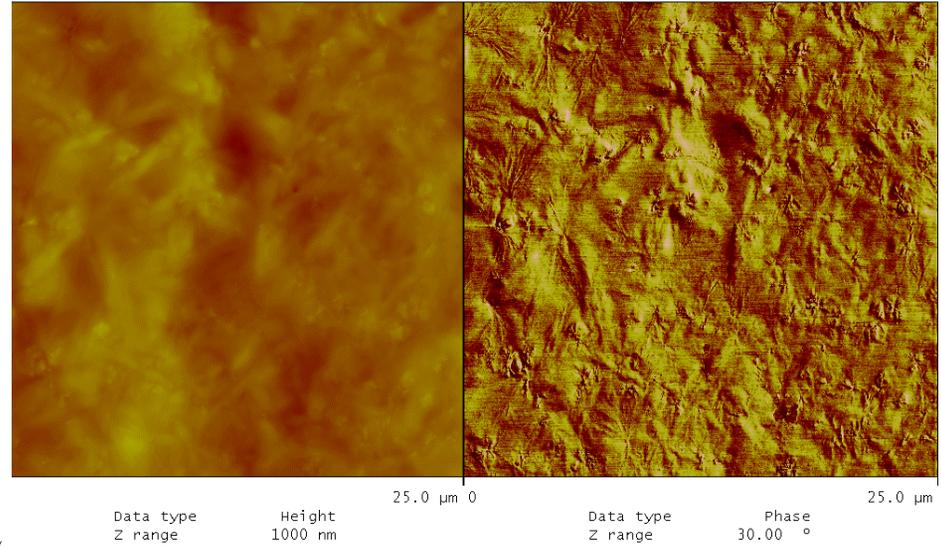
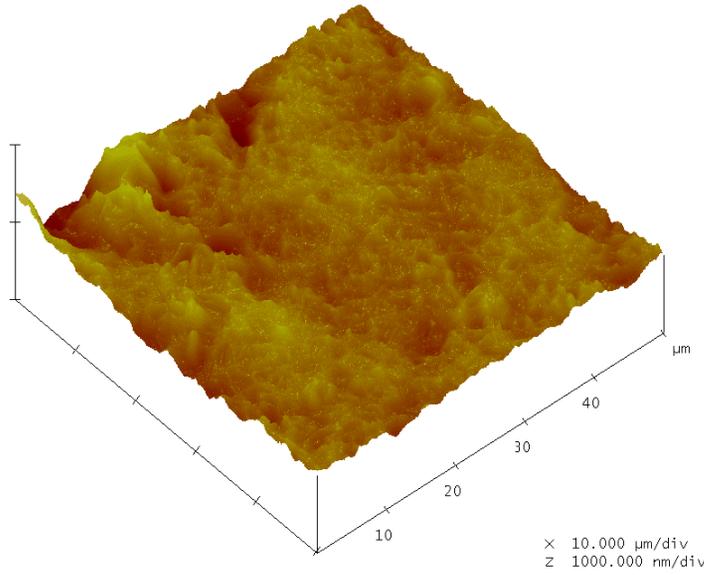


pf1r.f06

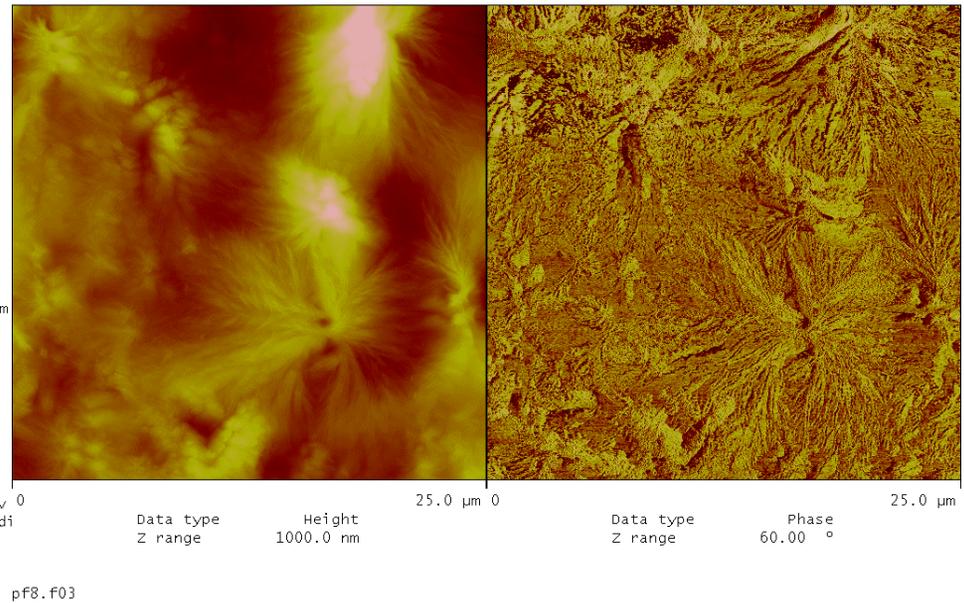
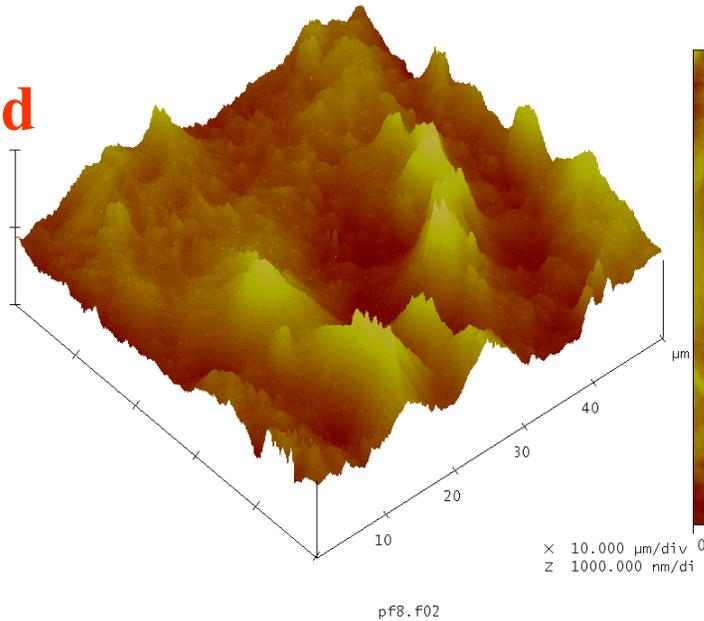
•Morphology of the area surrounding the holes has significantly changed.

PMMA-CO-PEA/PVDF: 70/30; Surface

Virgin



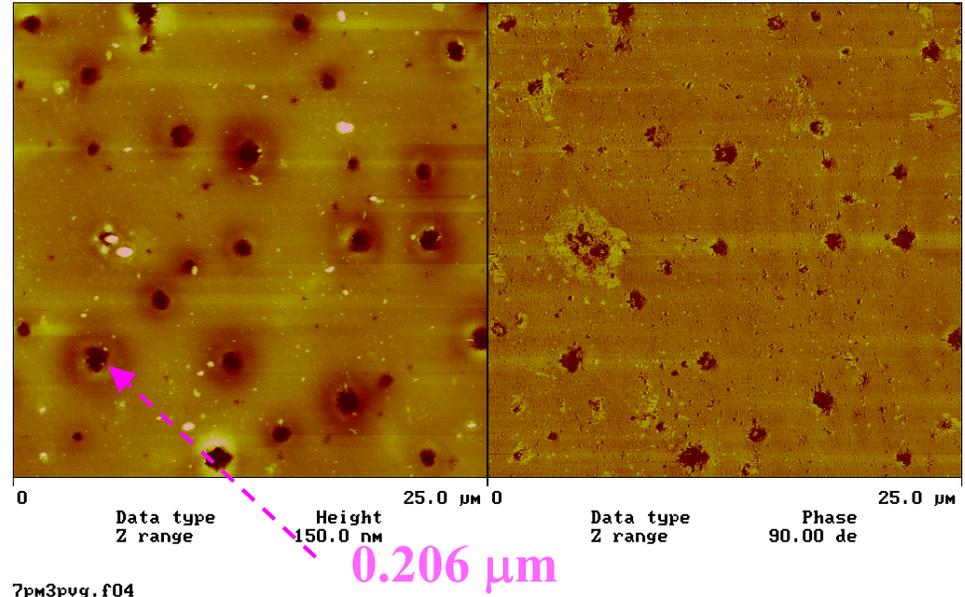
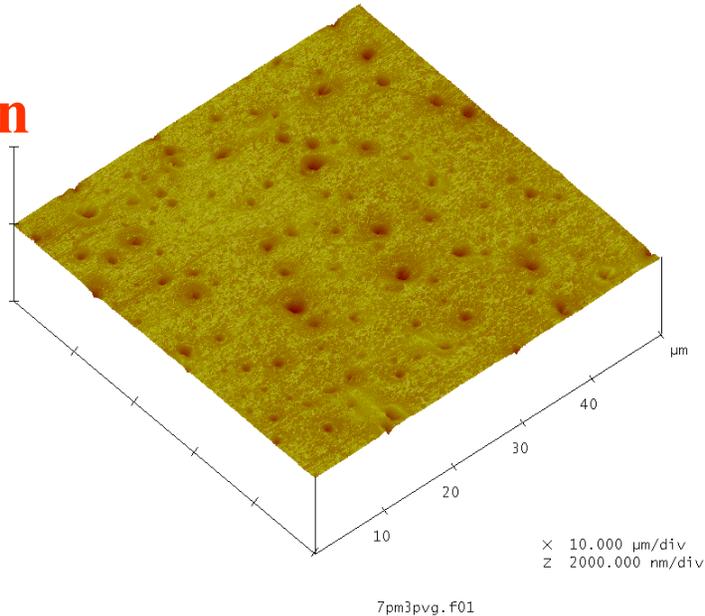
UV Exposed



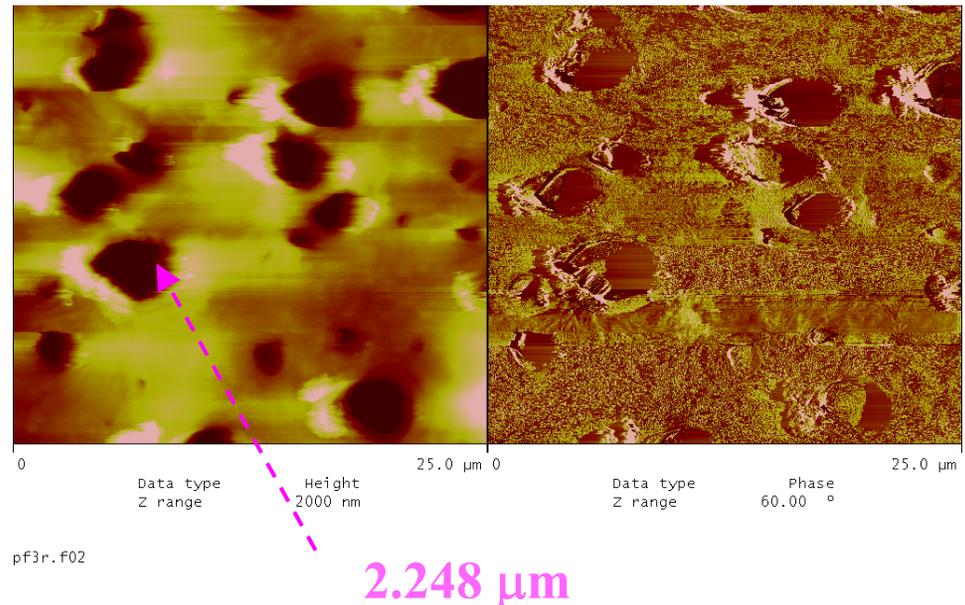
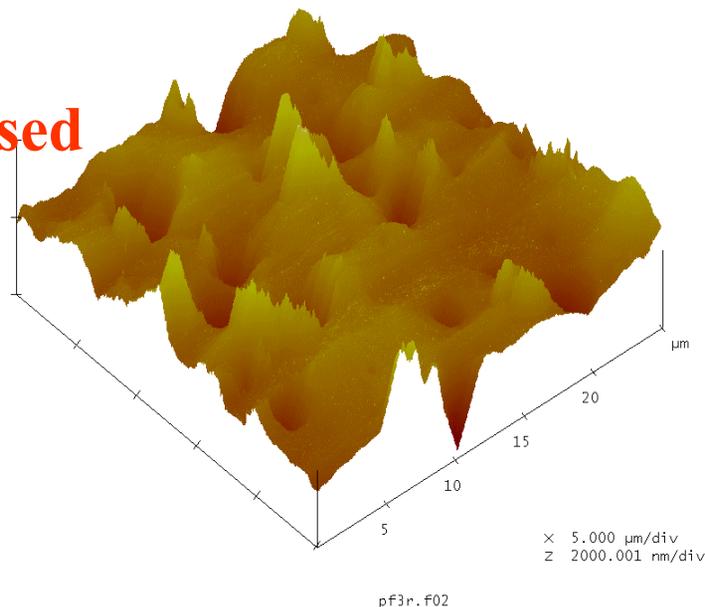
• Roughness is increased and crystal structures are more abundant.

PMMA-CO-PEA/PVDF: 70/30; Interface

Virgin



UV Exposed



• Roughness is increased and morphology has obviously changed.

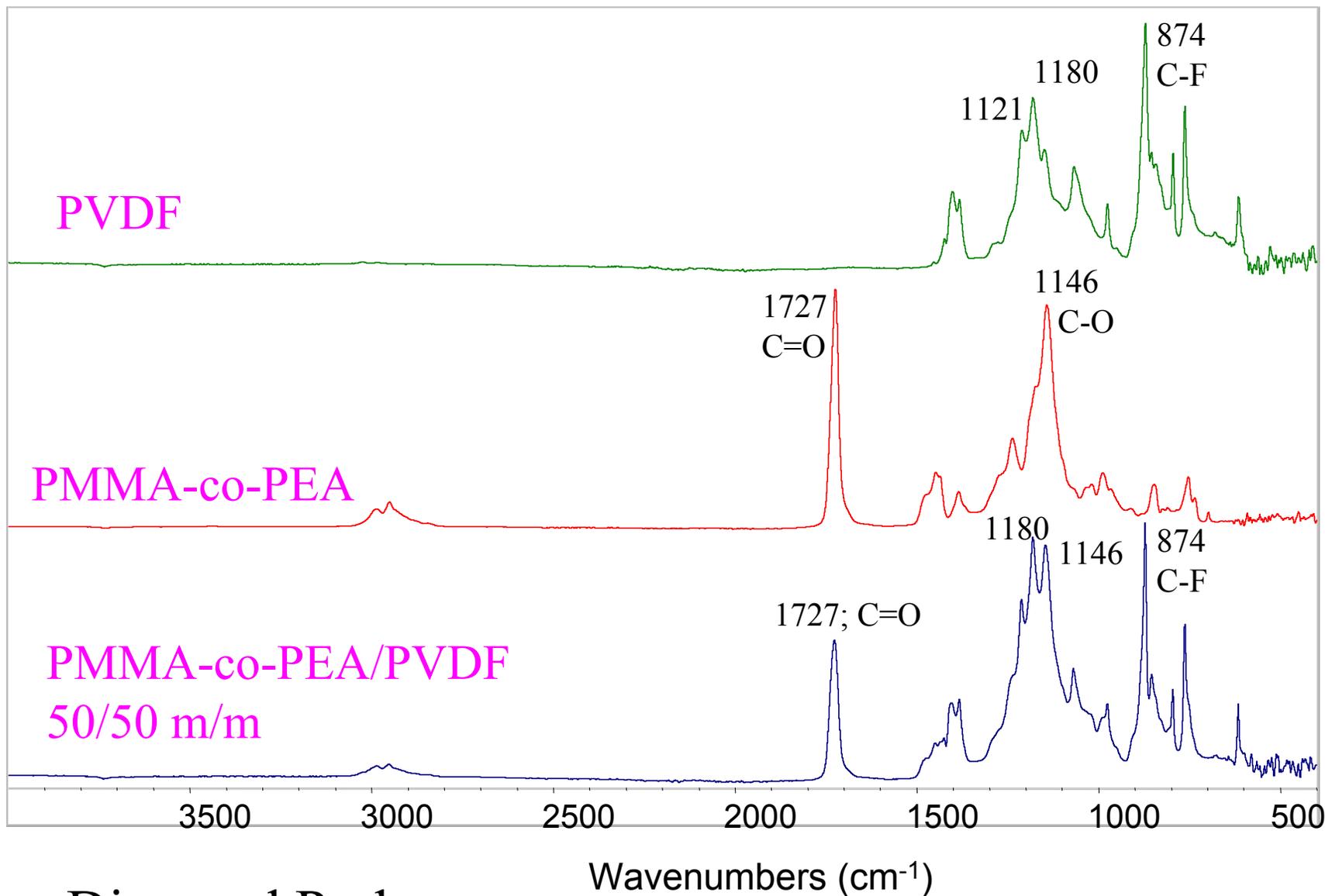
Other studies* on the PVDF blends using neutron scattering have also shown that the crystallinity increases after QUV treatment, which is consistent with our AFM results. This phenomenon might be due to the local movement, degradation of amorphous material, and/or rearrangement of the polymer chains during exposure to UV light at 50 °C.

*LP Sung et al. “Microstructure and Durability-related Physical Properties of Fluoropolymer Coatings”, Submitted to APS conference (2002).

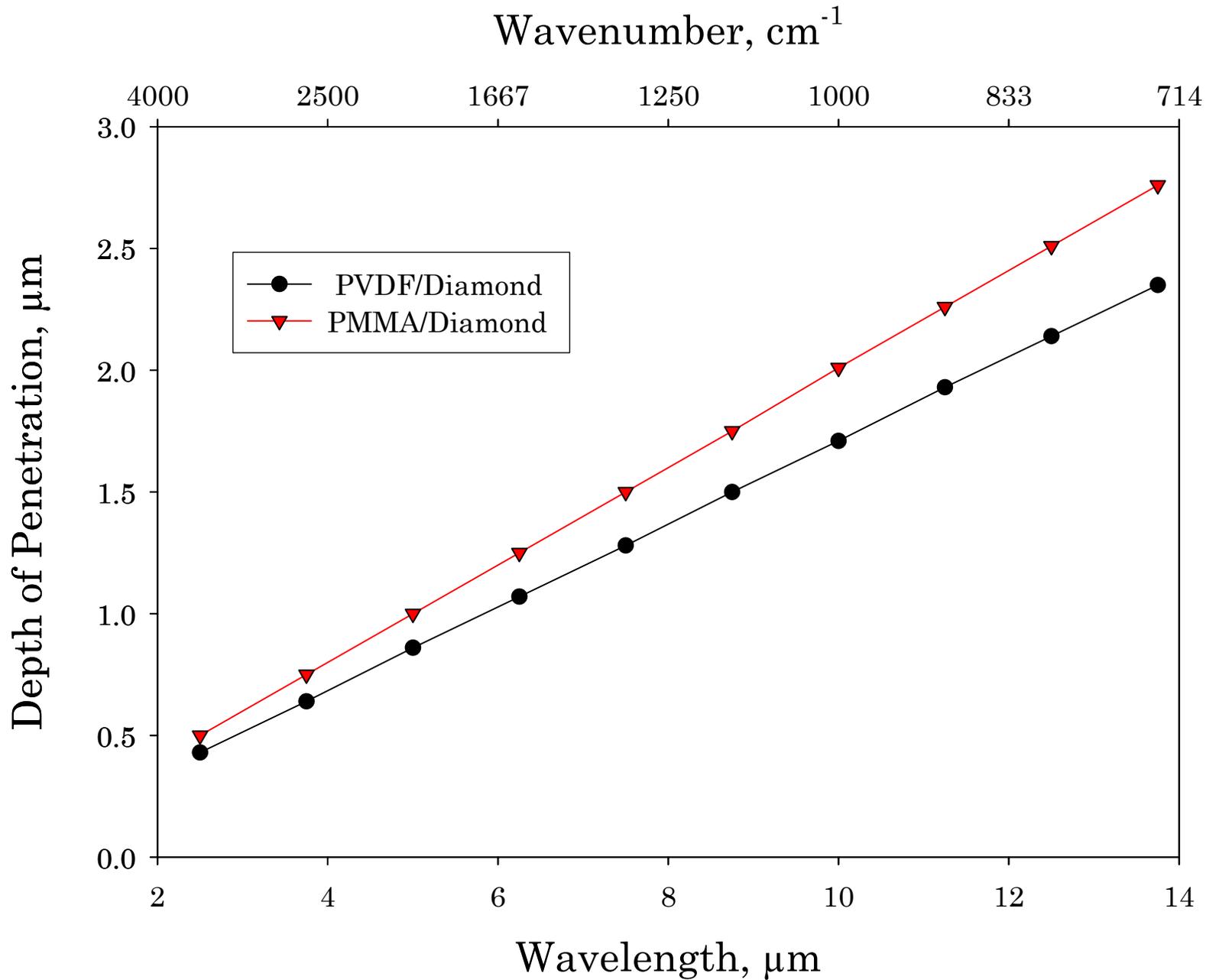
Effects of UV Exposure on Morphology of PMMA-co-PEA/PVDF Blends

Blends	Surface	Interface
PMMA-co-PEA/PVDF, 30/70, m/m	Topography: little change due to exposure; Morphology: more organized crystal structure after exposure	Roughness increased; Morphology: more organized crystal structure after exposure
PMMA-co-PEA/PVDF, 50/50, m/m	Topography: little change due to exposure; Morphology: more organized crystal structure after exposure	Roughness increased; Morphology: Substantial change
PMMA-co-PEA/PVDF, 70/30, m/m	Topography: roughness increased; Morphology: more organized crystal structure	Roughness increased; Morphology: Substantial change

FTIR-ATR Spectra of Unaged PMMA-co-PEA/PVDF Samples



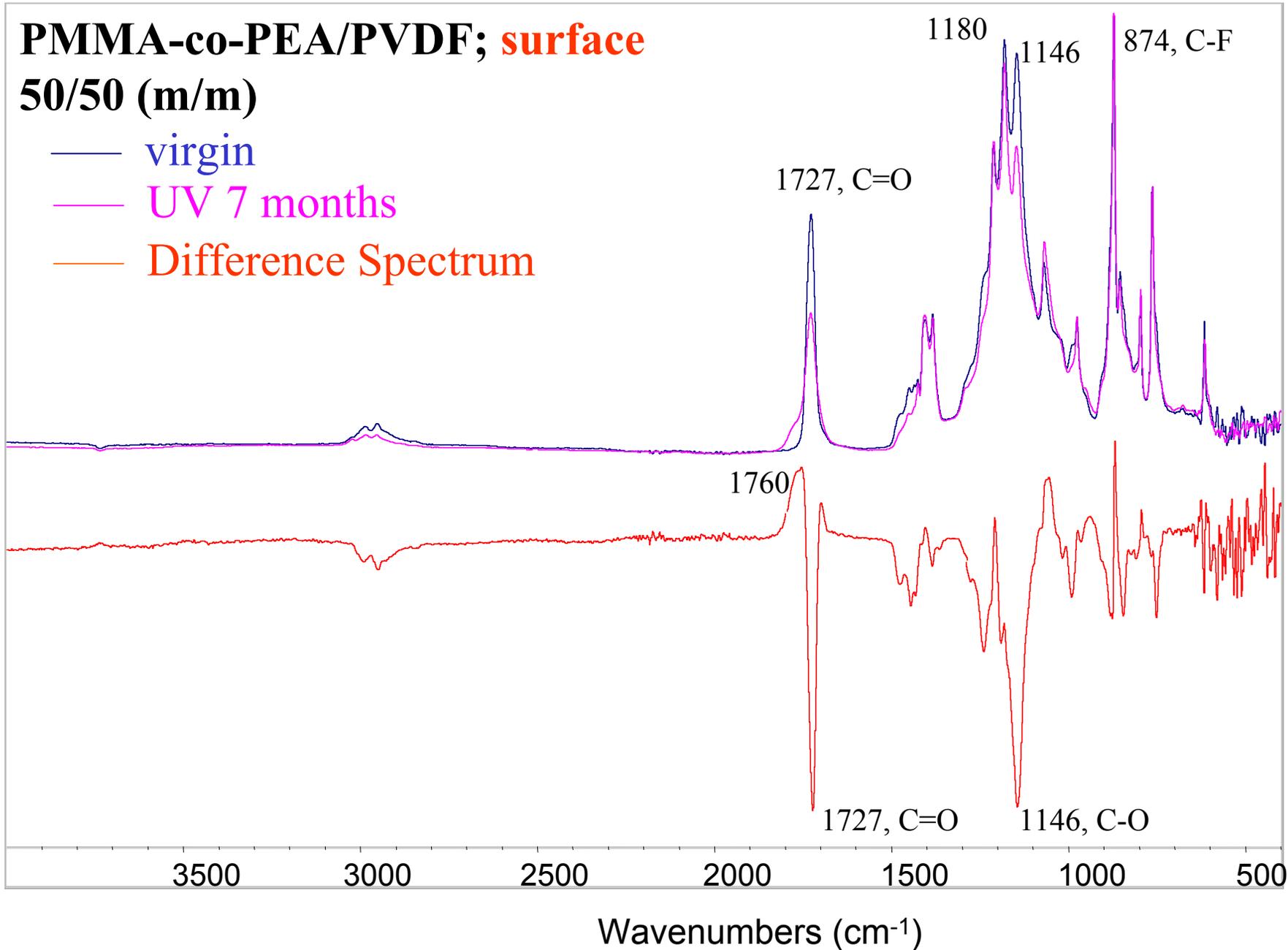
•Diamond Probe



PMMA-co-PEA/PVDF; **surface**

50/50 (m/m)

- virgin
- UV 7 months
- **Difference Spectrum**

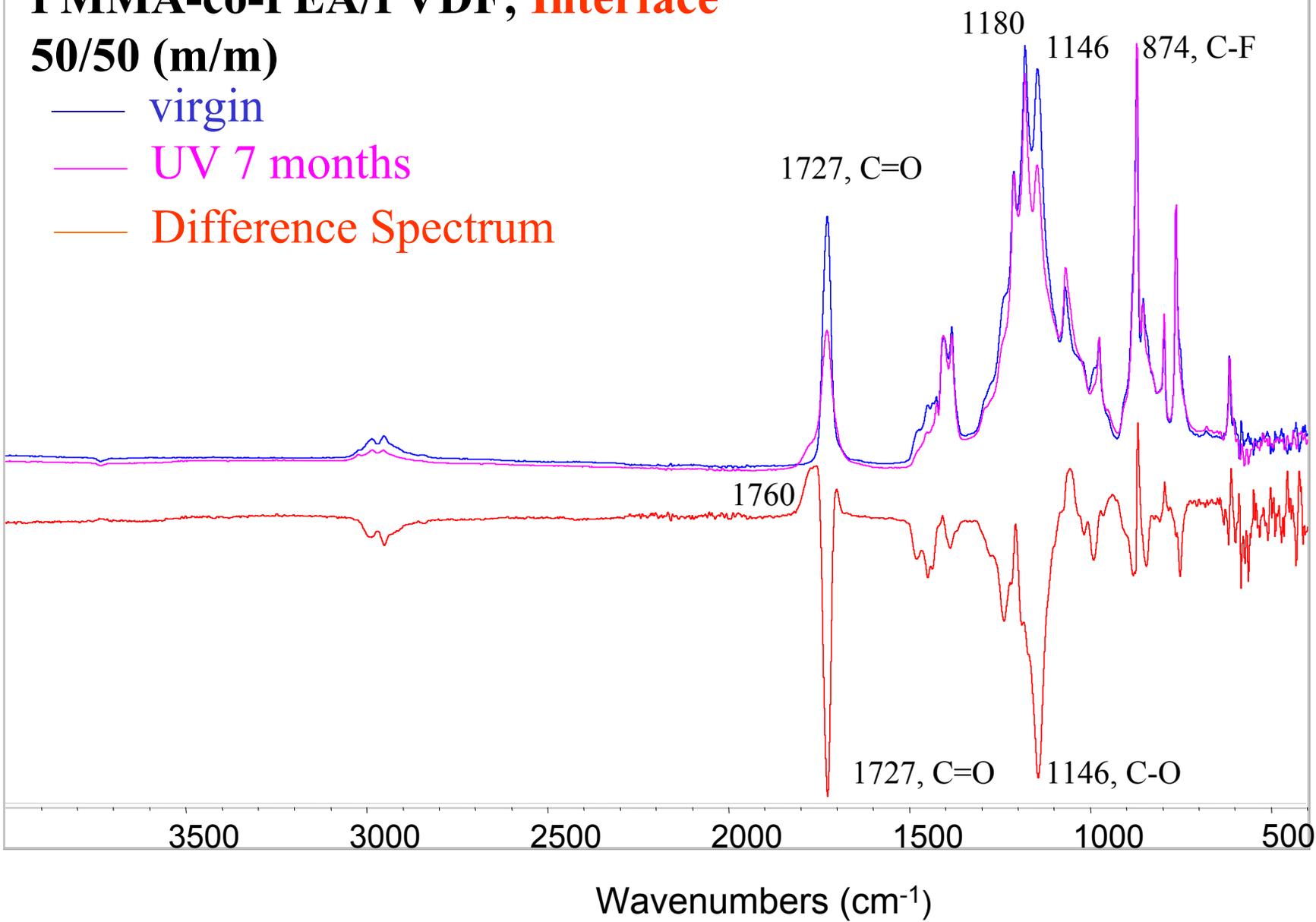


• ATR-FTIR

PMMA-co-PEA/PVDF; Interface

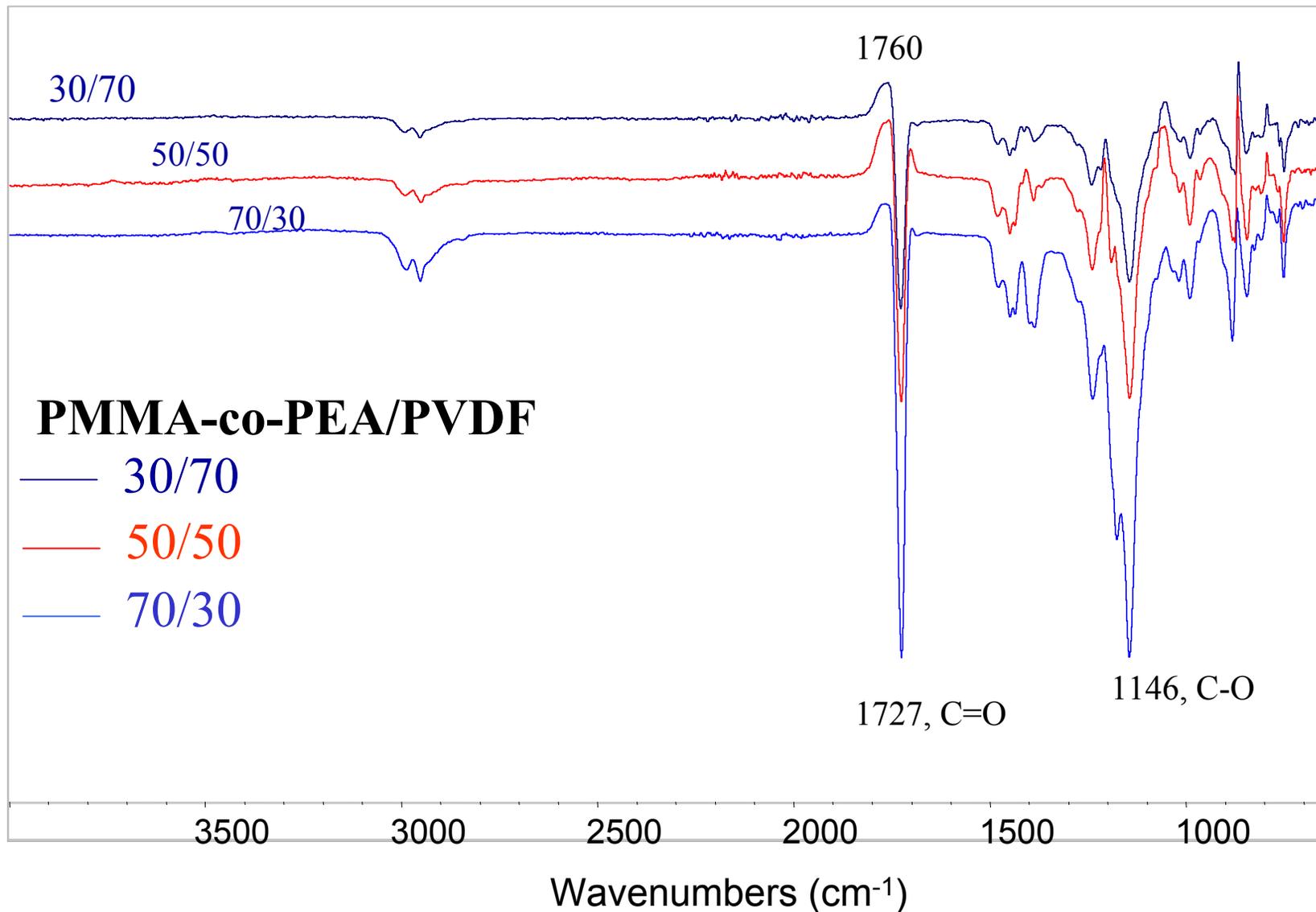
50/50 (m/m)

- virgin
- UV 7 months
- Difference Spectrum



•ATR-FTIR

ATR Difference Spectra of PMMA-co-PEA/PVDF (surface)



Effect of UV Exposure on Chemical Changes of PMMA-co-PEA/PVDF Blends

C=O/C-F FTIR Intensity (ATR)

PMMA-co-PEA/PVDF (m/m)	30/70		50/50		70/30	
Sample	Surface	Interface	Surface	Interface	Surface	Interface
Virgin	0.302	0.325	0.522	0.597	1.532	1.888
UV exposure for 7 months	0.125	0.123	0.301	0.314	0.525	0.816