Article

Polyvinylidene Fluoride Aerogels with Tailorable Crystalline Phase Composition

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Table S1. Detailed description of the prepared samples and their compositions

Sample	PVDF (wt.%.)	PVDF/H_2O	x_{DMF}	x_{EtOH}	t_{gel} (min)
P12	12	0	1	0	30
P9	9				45
P7	7				-
P5	5				-
P3	3				-
P12E0.2	12	0	0.8	0.2	21
P9E0.2	9				23
P7E0.2	7				27
P5E0.2	5				45
P12E0.4	12	0	0.6	0.4	15
P9E0.4	9				18
P7E0.4	7				25
P5E0.4	5				45
P12E0.5	12	0	0.5	0.5	10
P9E0.5	9				12
P7E0.5	7				15
P5E0.5	5				16
P12E0.2H0.75	12	0.75	0.8	0.2	3
P12E0.2H0.80		0.80			5
P12E0.2H0.86		0.86			8
P12E0.2H0.92		0.92			10
P12E0.2H1.0		1.0			10
P12E0.2H1.5		1.5			11
P12E0.2H3.0		3.0			13
P12E0.2H6.0		6.0			18

Table S2. Textural properties of the PVDF aerogels prepared using ethanol as nucleation agent

Sample	S_{BET} ($m^2\ g^{-1}$)[a]	Pore diameter (nm)[b]	Pore volume ($cm^3\ g^{-1}$)[c]	ρ_b ($g\ cm^{-3}$)[d]	ρ_s ($g\ cm^{-3}$)[e]	Porosity (%)
P12E0.2	113	19	0.54	0.125	1.49	92
P9E0.2	136	23	0.80	0.096	1.37	93
P7E0.2	160	21	0.86	0.086	1.58	94
P5E0.2	152	22	0.85	0.077	1.40	95

[a]Specific surface area obtained by N_2 sorption using the BET method
[b]Determined from the desorption curve using the BJH method
[c]Determined from the adsorption curve using the BJH method
[d]bulk density calculated by dimensions and weight
[e]skeletal density calculated using a He pycnometer

The relative content of the crystalline phases ($F(\alpha+\beta+\gamma)$) in the PVDF aerogels was calculated using the following equation [1]:

$$F(\beta+\gamma)=\frac{A_{\beta,\gamma}}{\left(\frac{k_{\beta,\gamma}}{k_\alpha}\right)A_\alpha+A_{\beta+\gamma}}*\ 100\%$$

Where A_α and A_β are the corrected baseline absorbance at 761 cm^{-1} and 840 cm^{-1}, respectively. k_α is $6.1x10^4 cm^2\ mol^{-1}$ and $k_{\beta,\alpha}$ is $7.7x10^4 cm^2\ mol^{-1}$ are the corresponding absorption coefficients. $F(\beta)$ and $F(\gamma)$ are calculated by using the intensity of the absorption peaks of 1275 cm^{-1} and 1234 cm^{-1}[2], for the β, and γ phases, respectively, according to the following equations:

$$F(\beta)=F(\beta+\gamma)*\frac{A_{1275}}{A_{1275}+A_{1234}}x*100\%$$

$$F(\gamma)=F(\beta+\gamma)*\frac{A_{1234}}{A_{1275}+A_{1234}}*\ 100\%$$

Finally, the relative content of α-PVDF ($F(a)$) was calculated using $F(a)=1-F(\beta)-F(\gamma)$.

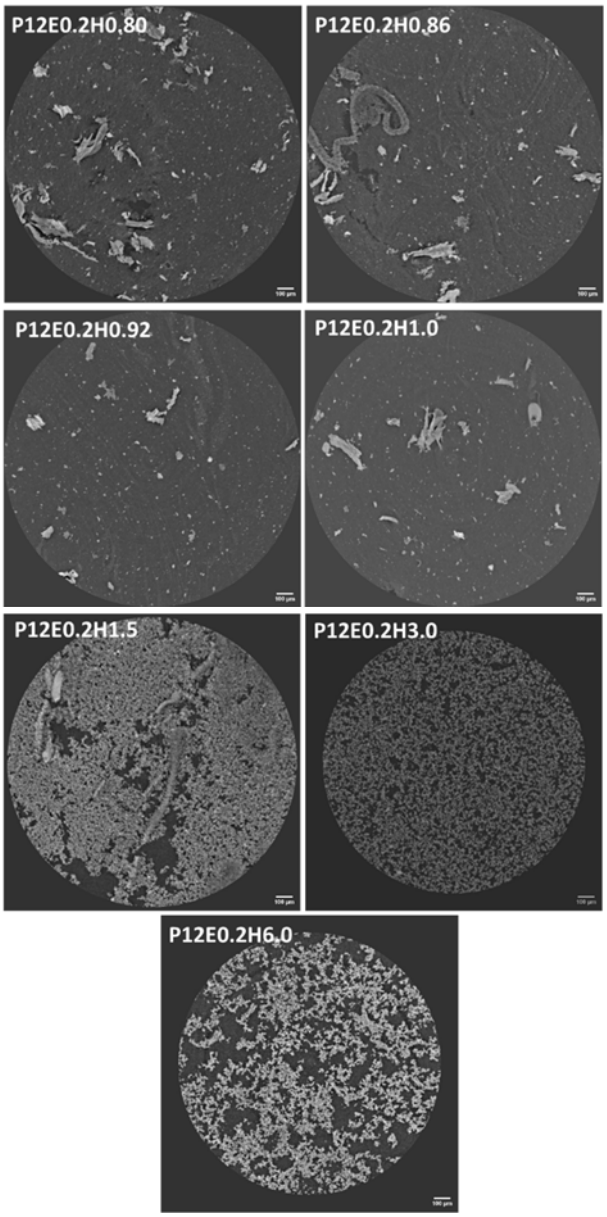

Figure S1. Axial maximum intensity projections (MIP) of the aerogels prepared with 12 wt.% PVDF, $x_{EtOH} = 0.2$, and variable PVDF/H_2O ratio from 0.80 to 6.0.

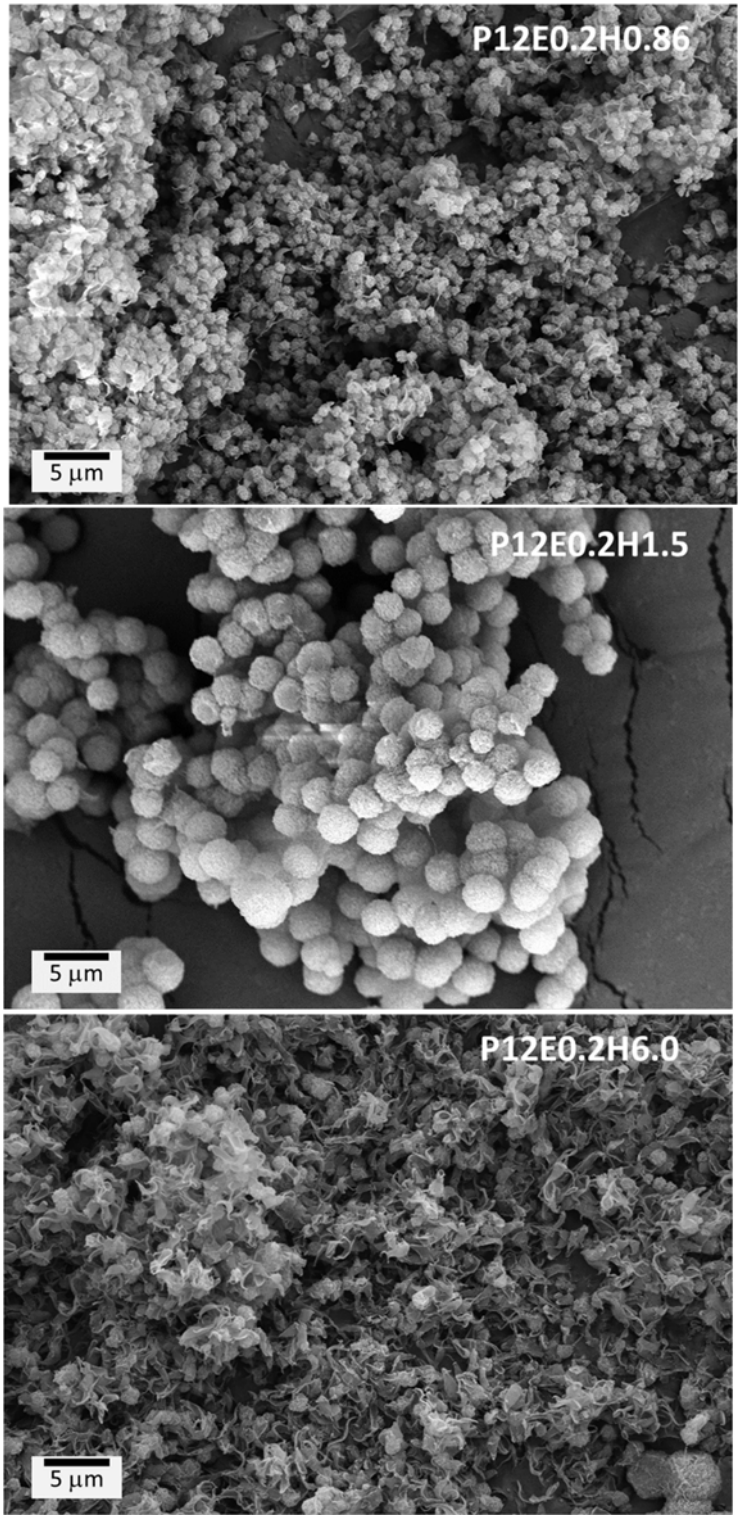

Figure S2. SEM micrographs displaying the morphological differences between the samples with variable phase composition. The P12E0.2 sample has a bimodal morphology of spherulites and leaf-like particles; the P12E0.2H1.5 aerogel has solely spherulites; the P12E0.2H6.0 has mostly leaf-like particles with small signs of tiny spherulites.

1. Zhou, H.; Wang, H.; Liu, Z.; Yang, H.; Yuan, C.; Wang, Y. Facilitated Phase Transformation of PVDF in Its Composite with an Ionic Liquid. *Polymer (Guildf).* **2021**, *220*, doi:10.1016/j.polymer.2021.123564.

2. Gregorio, Jr., R.; Cestari, M. Effect of Crystallization Temperature on the Crystalline Phase Content and Morphology of Poly(Vinylidene Fluoride). *J. Polym. Sci. Part B Polym. Phys.* **1994**, *32*, 859–870, doi:10.1002/polb.1994.090320509.