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Characterization

Characterizations of the pristine PVDF and dopamine functionalized PVDF polymer films were done using Fourier transform infrared spectroscopy (FTIR), Thermogravimetric Analysis (TGA), Raman Spectroscopy,

FTIR Spectroscopy

To verify changes in the structure of PVDF before and after dopamine functionalization, the infrared spectra of the pristine and modified PVDF polymer powders were obtained. The Perkin-Elmer system 2000 FTIR was used to characterize the polymeric films. The FTIR spectra were obtained with 8 scans per sample over the range of 4000 – 400 cm^{-1} with 4 cm^{-1} resolution.

Raman Spectroscopy

Raman spectra were obtained using Renishaw Invia Raman Microscope with 532 nm Nd: YAG laser.

Thermogravimetric analysis (TGA)

Prior to thermal analysis the samples were dried under vacuum at 60 $^{\circ}\text{C}$ for 24 h and subsequently were stored in a desiccator. TGA curves were recorded on a TA instrument mode 2950 in a temperature range of room temperature to 900 $^{\circ}\text{C}$ with a heating rate of 10 $^{\circ}\text{C}/\text{min}$. TGA runs were carried out on samples having typical weight of 10 - 20 mg.

Differential Scanning Calorimetry (DSC)

Differential Scanning Calorimetry measurements were carried out in TA DSC 2010 equipment containing thermal analysis software for data interpretation to investigate the changes in the thermal properties; the enthalpy of fusion and crystallization. In representative runs, 3-4 mg of samples in sealed standard pans were ramped from 15 $^{\circ}\text{C}$ temperature to 350 $^{\circ}\text{C}$ at heating rate of

2 °C/ min. To avoid oxidative degradation, the sample and reference pans were purged with nitrogen at a constant flow rate of 68 ml min⁻¹.

The heat of fusion (ΔH_f) was obtained from the area under the melting thermo gram. The crystallinity (X_c) in sample was obtained in Equation 1:

$$\%Crystallinity = \frac{\Delta H_f}{\Delta H_f(Crys)} \times 100 \quad (1)$$

ΔH_f is the heat of fusion of the sample and $\Delta H_{f(crys)}$ is the heat of fusion of 100 % crystalline PVDF and was taken as 104.7 Jg⁻¹. For PDOPA@PVDF, the percentage crystallinity was calculated by correcting the recorded ΔH_f dividing by the weight fraction of PVDF in the investigated sample.

Contact Angle Measurement

The water contact angle of the PVDF and the dopamine modified films were determined using an optical contact angle meter system (Dataphysics, OCA-20) at ambient temperature to study the hydrophobicity of the films. The modified PVDF films were stored for approximately one week after being prepared at room temperature in air prior to their contact angle analysis. The films were then placed on glass slides and fastened on both ends using Teflon tapes. At least five independent determinations at different sites of one sample were taken.

X-ray diffraction (XRD)

The crystal structure of the PVDF and the grafted films (different % of grafting) was determined by Bruker D8 discover GADDS X-ray diffractometer (XRD) (40 kV, 40 mA).