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Supporting Information

PVDF-MWNT interactions control process induced β-lamellae morphology and its orientation in the nanocomposites

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Table S1: The various amount of MB mixed with MWNTs and measured MB wt% adsorbed

 on to MWNTs as determined by TGA thermal analysis.

MWNTs (mg)	MB added mg / wt%	MB weight loss (%) from TGA
200	10.5 / 5	3.3
200	22.2 / 10	4.2
200	35.3 / 15	4.7
200	50.0 / 20	5.8
200	66.6 / 25	6.2
200	85.7 / 30	6.6
200	107.7 / 35	7.2
200	133.3 /40	8.2

The TGA thermogram of MWNT-MB π -complexes are shown in Figure S1a which shows the major degradation in the temperature range of 260 - 470 °C and very minor weight loss centred around 190 °C. Noticeably, the major weight loss increases with increasing adsorbed MB content while the minor one shows only marginal increase in % weight loss. The total MB content in the MWNT-MB π -complexes is varied from 3.3 to 8.2 wt%. Differential thermo-gravimetric (DTG) curves (Figure S1b) derivatized from TGA graphs (Figure 2a) shows that the major degradation peak shift towards the lower temperature with increasing amount of MB on MWNTs. This can be clearly seen in graph of dependence of peak T_d on the MB content as shown in Figure 2b. The peak T_d progressively decreases with increasing amount of MB coverage content. At 3.3 wt% MB content, MWNT-MB π -complex shows maximum peak T_d of ca. 380 °C and is decreased to a temperature of ca. 340 °C as the MB content increased to ca. 8.2 wt%. Noticeably, the peak T_d shows drastic variation in the MB concentration range between 3.3 to 6.2 wt% but further loading shows minimal effect on peak T_d. This result suggests that the extent of interaction of MWNT and MB is highly dependent on the concentration of MB on MWNTs surface. In other words, lower the MB content on the MWNT surface, the stronger the interaction between the two and vice-versa.



Figure S1: (a) TGA thermogram (b) differential thermal gravimetric (DTG) graphs of MWNT-MB π -complexes and (c) the variation of peak degradation temperature (T_d) with MB coverage content.

Figure S2a shows UV-Vis spectra for various MWNTs. Pure MB shows absorbance peak at 656 nm and a shoulder peak at 609 nm which are characteristics of MB monomer and dimer in solution respectively.⁴¹ The MB monomer absorption peak at 656 nm is reported to occur due to π - π * transition and is shifted to lower wavelength upon π -complexation with MWNTs. More interestingly, the position of absorption peak is systematically shifted towards lower wavelength with decreasing MB coverage content while the shoulder peak is not clearly seen especially when MB content is 6.6wt% and below. The variation of adsorbed MB content with the wavelength of absorption peak wavelength is plotted in Figure S2b which clearly shows that the absorption peak wavelength is linearly decreasing MB content while MB content of 7.2 wt% registers 648 nm which is closer to the absorption value of free MB monomer for such transition. The change in the π - π * transition energy (wavelength) of MB

monomer by π -complexation with MWNTs is attributed due to transfer of charge from MWNTs to π^* level of MB which resulted in supressing the π - π^* transition of MB monomer. This is evident from the Figure S2b that MB molecules at lower concentration tend to receive more charge from MWNTs hence require more energy (lower wavelength of absorption) for π - π^* transition as compared to that of MB molecules at higher coverage concentration. This clearly demonstrates that the extent of interaction (between MWNT and MB) not only be modified by MB adsorption but also be systematically controlled by the MB coverage. These results are well in accordance with the TGA analysis discussed in the previous section.



Figure S2: (a) UV-vis spectra of MWNT-MB π -complexes at various MB coverage content and (b) the dependence of wavelength as function of MB coverage concentration.



Figure S3. Comparison of FT-IR spectra of (a) as pressed and (b) rolled neat PVDF, PVDF+2% MWNTs and PVDF+2% MWNT-MB nanocomposites.



Figure S4: The variation of polar phase content with MB content adsorbed on to MWNTs.