

Supporting Information

Unravelling the sub-nanosopic structure at interphase in Poly (vinyl alcohol)-MOF nanocomposite and its role on thermo-mechanical properties

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1. SEM and FTIR of ZIF-8

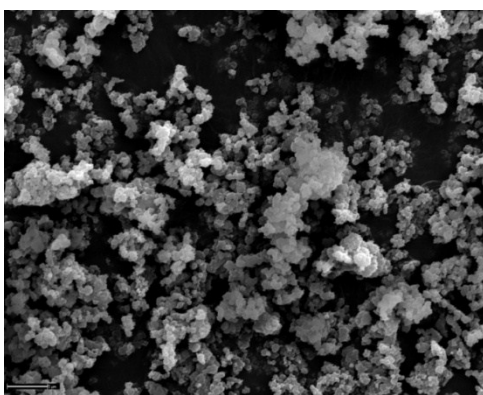


Figure S1. SEM micrograph of ZIF-8. The scale bar on the bottom (left side) is 5 micrometer.

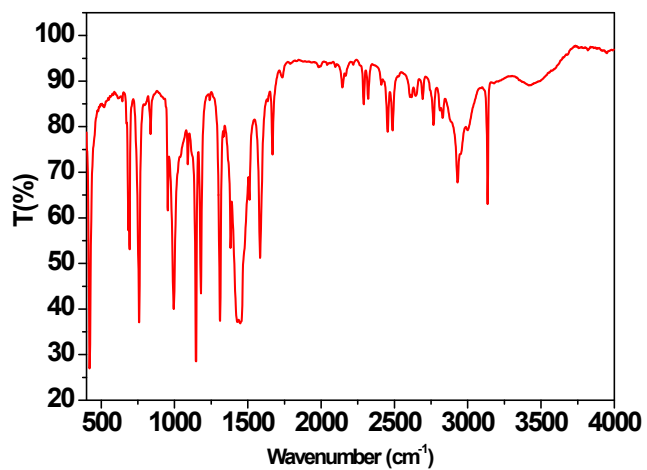


Figure S2. FTIR spectrum of ZIF-8

2. SEM of surface of pure PVA and PVAxZ nanocomposites

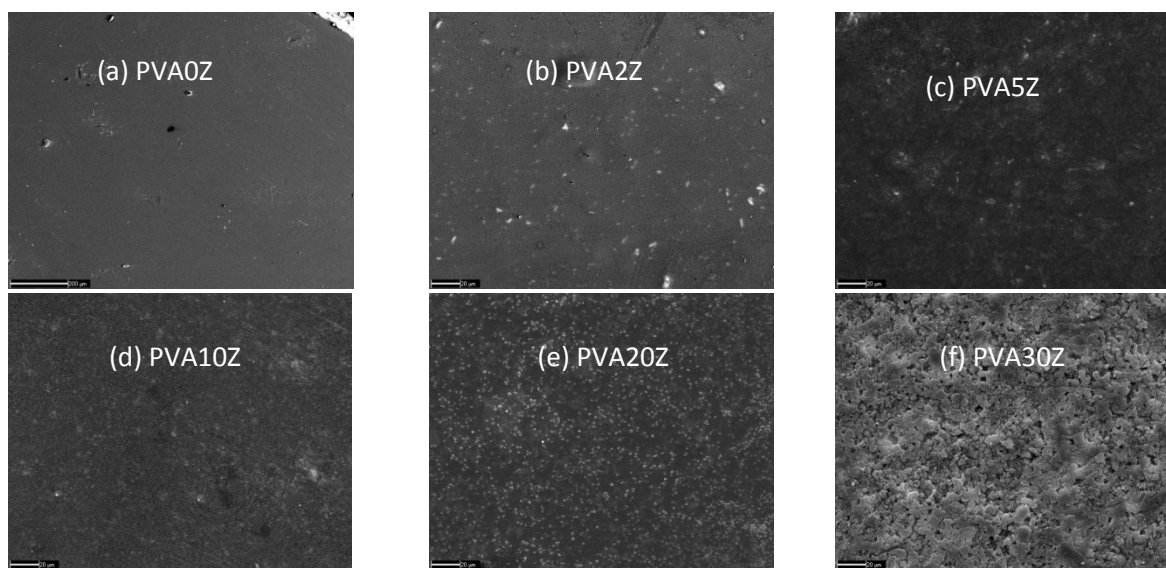
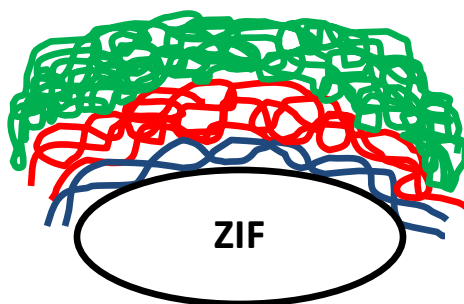


Figure S3(a-f) SEM back scattering electron images of the surface of PVA and the nanocomposite films. The scale bar shown at the left side bottom of the images is 20 micrometer

3. FTIR of pure PVA and PVAXZ nanocomposites

Figure S3(a-f) shows the ZIF-8 particles distribution in the PVA matrix wherein it is clearly seen that up to 20 wt.% ZIF particles are uniformly distributed and on further loading i.e. 30 wt.% aggregation of ZIF-8 occurs in the PVA matrix. It indicates that 20 wt.% of ZIF-8 is close to the percolation threshold in PVA matrix. On loading of ZIF-8 in PVA, the FTIR peaks have contribution from three types of functional groups viz. (Type 1) which have interaction within PVA matrix similar to pure PVA and these are not affected by the presence of ZIF (Bulk layer); (Type 2) which are present at the interfacial region and having direct interaction with the functional groups present at the ZIF particle's surface (Type 3) which are present at the interphase region wherein the hydrogen bonding has been disrupted but they do not interact directly with the ZIF particles. The polymer chains with functional groups taking part in types 2 and 3 constitute the interphase in these nanocomposites and primarily affect the FTIR spectrum. With the increase in loading of ZIF particles, the inter-particles distance reduces up to 20 wt.% as observed from SEM micrographs. In such a scenario, it appears that nearly all the polymer chains directly interact through one or more interaction points with the ZIF's functional group and contribution from type 3 functional groups enhances drastically reducing the contribution from other type of functional groups. As a result, the FTIR spectrum for PVA20Z is drastically different from other PVAXZ sample. This is also supported by the DSC results which show that molecular packing of whole PVA matrix is altered at this loading indicating the absence of the bulk type layer. Due to aggregation at highest loading (30 wt.%), the inter-particle distance increases and again the contribution of type 3 functional groups is suppressed leading to the observed changes in the FTIR spectrum.



Scheme S1: Green, Red and Blue colour polymer chains represent the chains having type 1, 2 and 3 function groups.

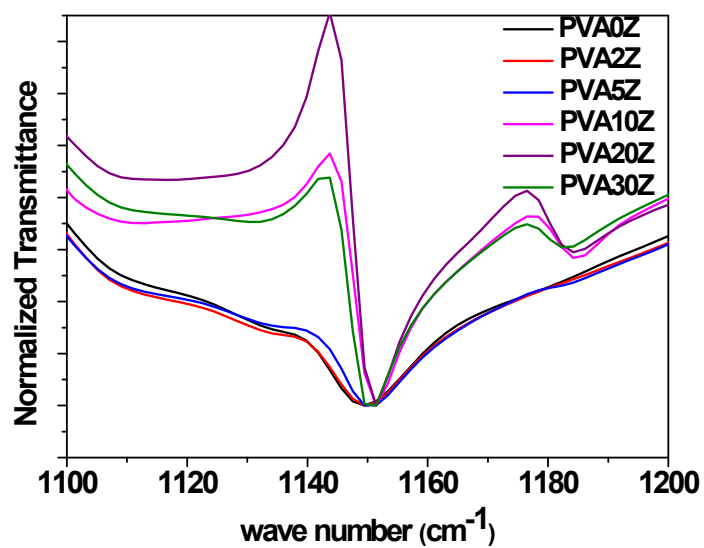


Figure S4: FTIR spectra showing the changes at C-O stretching vibrational mode

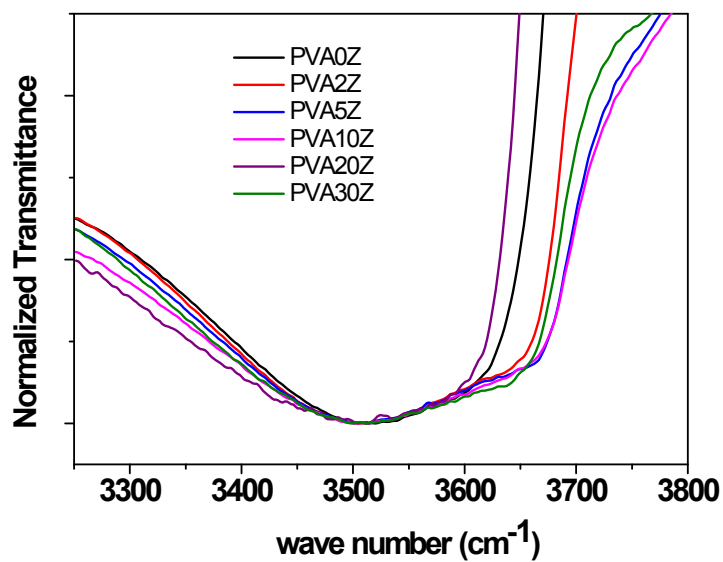


Figure S5: FTIR spectra showing the changes at broad hump corresponding to hydrogen bonded O-H stretching

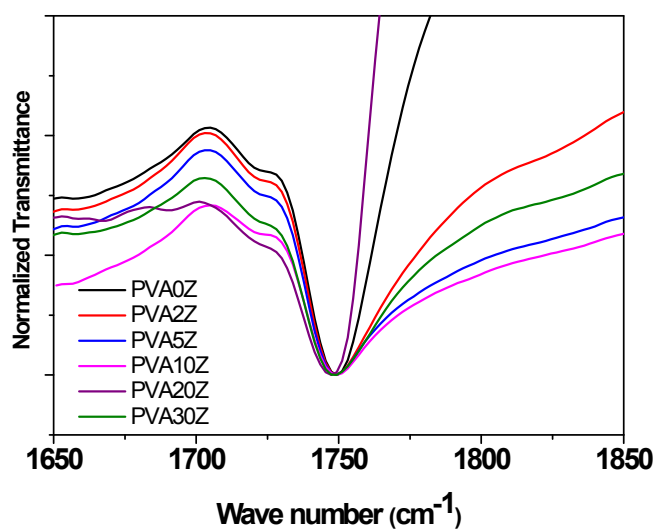


Figure S6: FTIR spectra showing the changes at vibrational mode of C=O

Table S1. Two *o*-Ps lifetime components (τ_3 and τ_4) from four component analysis with first component (τ_1) fixed at 125 ps. Four component fit was not possible for PVA0-5Z composites. τ_{av} and I_{total} are calculated as follows

$$\tau_{av} = (\tau_3 I_3 + \tau_4 I_4) / (I_{total})$$

$$I_{total} = (I_3 + I_4)$$

Sample	τ_3 (ns)	I_3 (%)	τ_4 (ns)	I_4 (ns)	τ_{av} (ns)	I_{total} (%)
PV-0Z	1.46±0.01	21.9±0.2	-----	----	1.46±0.01	21.9±0.2
PV-2Z	1.48±0.01	21.6±0.2	-----	-----	1.48±0.01	21.6±0.2
PV-5Z	1.48±0.01	21.3±0.2	-----	-----	1.48±0.01	21.3±0.2
PV-10Z	1.31±0.05	19.9±0.8	2.68±0.24	3.6±1.1	1.51±0.50	23.5±1.9
PV-20Z	1.20±0.07	16.7±1.0	2.40±0.12	7.9±1.4	1.58±0.33	24.1±1.7
PV-30Z	1.16±0.03	15.9±0.5	2.60±0.08	8.9±0.9	1.67±0.22	24.8±1.0