Optimization of Nanoclay Concentration for the preparation of suitable nanohybrid:

Nanohybrids have been prepared with a series of nanoclay concentration mixed with PVDF matrix ranging from 1 to 10 wt% of nanoclay through solution route. The stress strain curves of all the nanohybrids have been shown below. The numbers after NH indicate the nanoclay concentration in nanohybrids.
It is clearly seen that the elongation at break increases systematically up to 4wt% followed by gradual decrease of elongation at break with further increasing the nanoclay concentration showing highest elongation for 4wt% nanohybrid. Further, the modulus of the nanohybrids increase consistently up to 8 wt.% of nanoclay followed by decrease of modulus for 10wt% of nanoclay.

Interestingly, toughness as measured from the area under the stress-strain curve systematically increase up to 4wt% of nanoclay in nanohybrid followed by drastic decrease with further increase of nanoclay concentration in nanohybrids indicating highest toughness is exhibited in 4 wt% nanohybrid.
So, from the above discussion it is evident that 4 wt.% nanoclay containing nanohybrid shows highest toughness, moderate stiffness and greatest elongation at break which makes it suitable for optimised nanohybrid. This superior behaviour of 4 wt% nanohybrid prompts us to use the particular concentration and we used the best nanohybrid for structural and other property improvement.
Figure S1 shows the optical micrographs of PVDF (P) and nanohybrids prepared through solution route (NH) films before and after stretching (numeric values indicate draw ratio) which are heat treated up to melting point (~180.0 °C). Just before melting, stretched nanohybrid film is squeezed quite less as compared to stretched PVDF film indicating residual very less residual stress in nanohybrid vis-à-vis PVDF. This is because the energy was spent to orient / align the needle-like crystallite in NH during stretching as similar energy was employed during stretching both for PVDF and NH. The β–phase in presence of nanoclay after stretching is responsible for this change. Stretched β phase PVDF regain its α phase after melting the film. But in nanohybrid, β phase generated by stretching the polymer chain which is again forming the same phase after melt quenching/crystallization.

**Figure S1:** Optical micrographs of pure PVDF (P) and its nanohybrid (NH) with indicated draw ratio (numeric value within the bracket) before and after heat treatment. The pristine PVDF (P) and pristine NH have been indicated by “0”. The dimension of the film was 1×1 cm² used for heat treatment.
FTIR spectra of PVDF, NH-m and NH-s are shown in Fig. S2. It supports the XRD results that solution cast nanohybrid (NH-s) has more β phase content as well as less content of α phase in comparison to melt extruded nanohybrid (NH-m).

![FTIR spectra of PVDF, NH-m and NH-s](image)

**Figure S2:** FTIR spectra of thin pure PVDF, its nanohybrid melt (NH-m) and solution processed (NH-s). The dash lines are showing peak positions of α, β and γ-phases of PVDF. The peak at 510, 600 and 840 cm$^{-1}$ represent β-phase. The peak at 811 cm$^{-1}$ shows the γ-phase and α peak at 615 cm$^{-1}$ whose intensity decreases for nanohybrids. The peak intensity of β-phase has increased for NH-s as compared to NH-m.

The first heating curve (DSC thermogrammes) of PVDF and its nanohybrid is shown in Fig. S3. PVDF shows characteristic curve of α phase whereas NH-m has higher melting point showing formation of β-phase in presence of nanoclay. In NH-s, further signature of higher melting point shows more β-phase in solution processed nanohybrid.
**Figure S3:** DSC thermograms of pure PVDF, melt (NH-m) and solution processed (NH-s) nanohybrid.

**Figure S4:** Stress-strain curves of (a) pure PMMA, PMMA nanohybrid melt (PMMANC-m) and solution processed (PMMANC-s) and (b) stress-strain curves of polyurethane nanohybrids melt (PUNH-m) and solution (PUNH-s) processed.
Figure S5: Deconvolution of XRD patterns of thin films for (a) pure PVDF and (b) PVDF nanohybrid solution casting (NH) at different draw ratio mentioned at a elongation rate of 5 mm/min. Numeric values after dash represent draw ratio.
Figure S6: XRD patterns of thin pure PVDF, its nanohybrid melt (NH-m) and solution processed (NH-s).

Figure S7: FTIR spectra of pure PVDF (P) and its nanohybrid (NH) at different draw ratio (Final length/Initial length) numeric terms denote draw ratio at a temperature of 90°C and draw rate of 5 mm/min. Pure PVDF shows only α to β conversion while nanohybrid shows α/γ to β transformation. The γ-phase peak gradually decreases with increasing draw ratio.
**Figure S8:** (a) $\alpha$ fraction as a function of draw ratio of PVDF and its nanohybrid (NH). (b) Amorphous fraction as a function of draw ratio of thin film for pure PVDF and its nanohybrid (NH). (calculated from deconvoluted XRD patterns; Fig. S5).