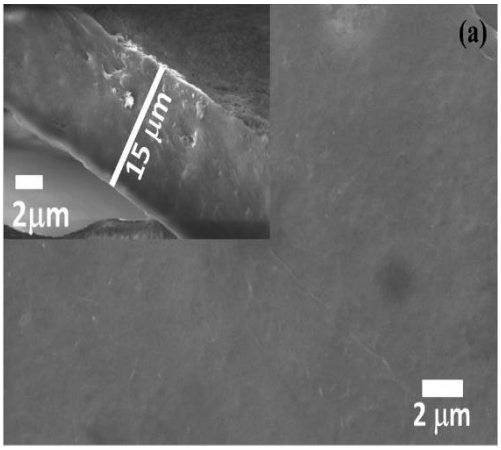
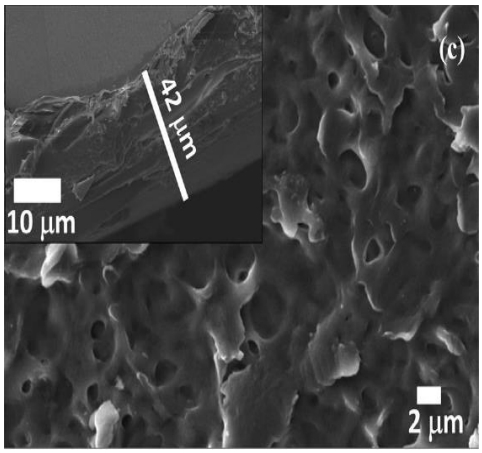
4. Material characterization of PVDF composites

4.1. Scanning electron microscopy (SEM) analysis

The surface morphology and cross sectional view of those prepared films recorded by a CARL ZISS (EVOLS 10) scanning electron microscope operated at 25 kV. Figure 4.1 (a-d) showing surface view of PVDF and its composites along with their cross sectional views in their corresponding insets. From the top view, it is observed that surface of PVDF is quite smooth. From those images, it is also apparent that surface morphology of PVDF has been diverted greatly after inclusion of fillers like ZnO and/or GO. From SEM images, it is evident that after ZnO or GO reinforcement, composites become more rough and porous. Hence interfacial defects become more prominent after filler incorporation. Also, modulation in interfacial polarization becomes apparent. Thus abundance in interface and defects in PVDF composites modifies the functional characteristics of PVDF to make them further suitable for ferroelectric applications.





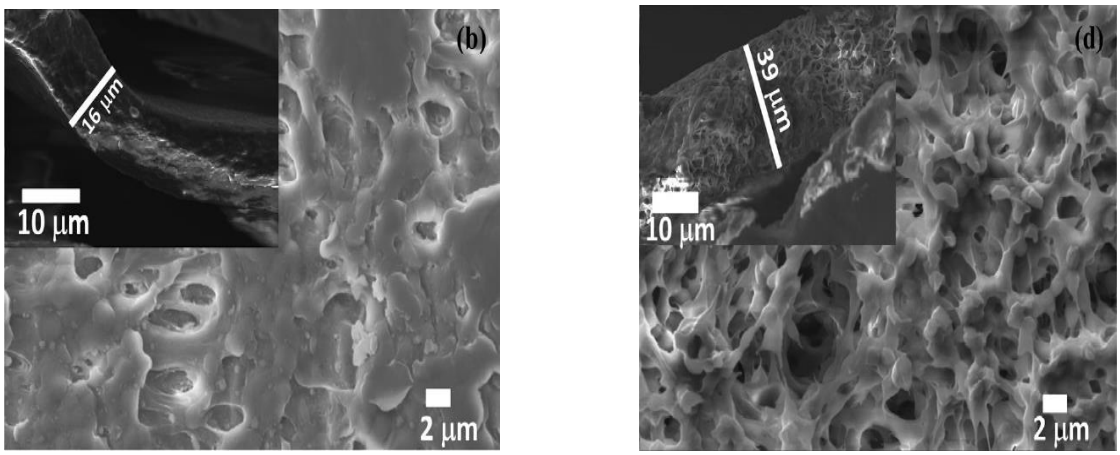


Fig. 4.1 Scanning electron microsopic (SEM) images for surface morphology and cross-sectional view of (a) PVDF, (b) PVDF/ZnO, (c) PVDF/GO and (d) PVDF/ZnO/GO films

4.2. X-ray diffraction (XRD) analysis

X-ray diffraction (XRD) pattern of PVDF and its various composites PVDF/ZnO, PVDF/GO and PVDF/ZnO/GO are recorded by X-ray diffractometer (PANalytical X'Pert Pro) with characteristic X-ray beam of CuK_α line (λ=1.54 Å) and are shown in fig. 4.2. There is a distinct peak at ~ 20^0 is observed in all of those membranes, which is assigned to β crystalline phase of PVDF. This peak arises due to reflection from (110) and (200) planes of orthorhombic β PVDF [167]. Additionally there is another small peak at ~ 18^0 is observed which is attributed to monoclinic α - phase due to reflection from (100) planes of PVDF ensuring presence of little amount of α- phase also [168]. After inclusion of ZnO, GO, and ZnO/GO peak position remains unaltered, which ensures formation of different composites. Also, after incorporation of various nanomaterials into host, PVDF peak becomes little sharper indicating better crystallinity of PVDF those composites. Since formation of PVDF completely in β - phase is difficult, abundance of crystalline β-phase in PVDF and its composites may aid in ferroelectric applications [169]. However presence of ZnO and GO is not confirmed from XRD analysis may be due to very little presence of them.

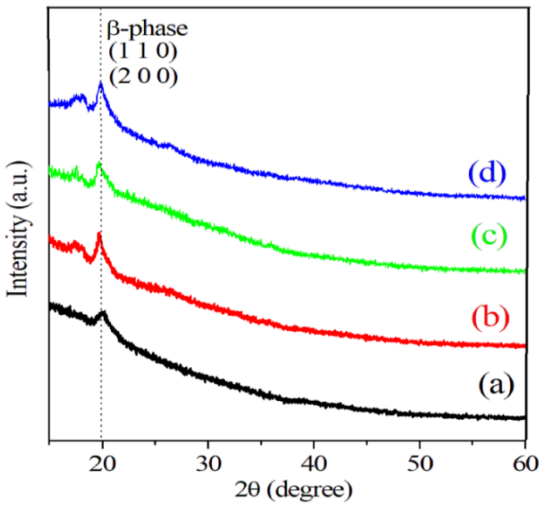


Fig. 4.2 XRD pattern of (a) PVDF, (b) PVDF/ZnO, (c) PVDF/GO and (d) PVDF/ZnO/GO films

XRD pattern of PVDF and its GO filled composites with varying concentrations are shown in fig. 4.3. All of those prepared membranes showing diffraction peak at ~ 20.2^0 confirms their formation in β crystalline form. This fact also ensures that after GO filler inclusion into the membrane, no such structural deformation has occurred. Additionally there is another peak at ~ 18.2^0 indicating presence of small amount of α - phase also. Although no separate peak for GO is identified but after GO inclusion into those membranes, peaks become little sharper which ensures better crystallinity of those composite membranes.

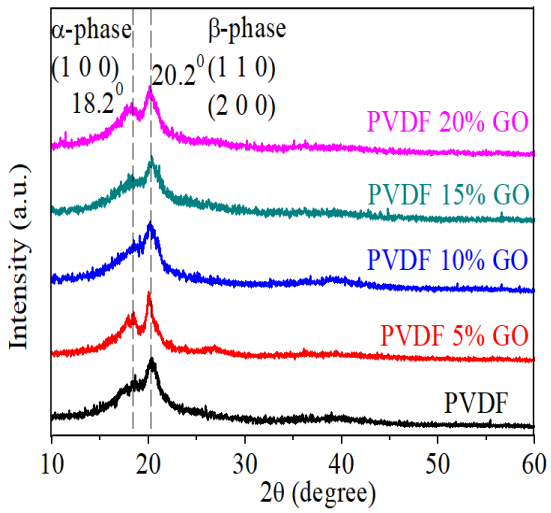


Fig. 4.3 XRD pattern of PVDF and its GO filled composite films with varying GO amount

4.3. Fourier-transform infrared (FTIR) spectroscopic analysis

4.3.1. FTIR analysis of PVDF composites

Fourier-transform infrared (FTIR) spectroscopic technique is usually used to achieve proper insight of bonding environment of any substance through absorption band spectrum of infrared (IR) radiation passed through it. Identification of bonding environment allows us to detect different crystalline phases present in a sample. FTIR spectra of all polymer composites are presented in fig. 4.4.

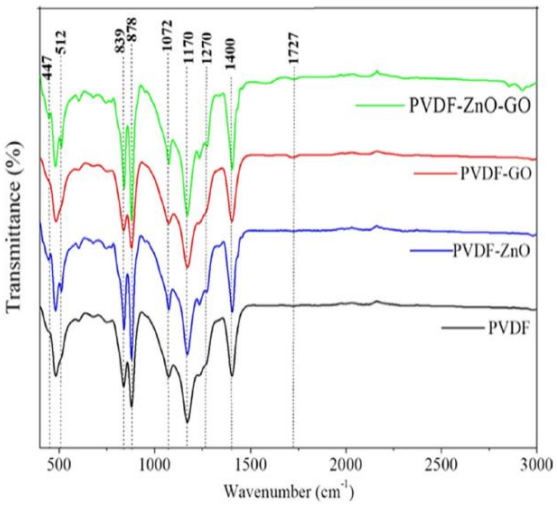


Fig. 4.4 FTIR spectra of PVDF and its composite films

Typical absorption bands which are characteristic feature of PVDF seems to be present in the spectra. Strong absorption bands located at 839 and 878 cm^{-1} are assigned to H-C-H rocking and F-C-F asymmetric stretching mode vibration respectively [170]. There are some common absorption peaks located at 1072, 1170, 1270 and 1400 cm^{-1} in all of those films arising due to C-C asymmetric stretching mode, F-C-F symmetric stretching mode, C-F out-of-plane deformation, and H-C-H wagging vibration respectively which are characteristic features of PVDF [171-172]. Presence of these absorption bands in all of those composites implying that after forming

composites PVDF has gone through no structural changes. A weak absorption peak at 1727 cm^{-1} is observed in PVDF/GO and PVDF/ZnO/GO composites which is characteristic of C=O stretching mode vibration of small amount of carbonyl and carboxyl group present there in GO [173]. An additional weak absorption peak at 447 cm^{-1} is observed only in PVDF/ZnO and PVDF/ZnO/GO which arises due to Zn-O stretching mode of vibration ensuring presence of ZnO there which were not confirmed earlier from XRD spectra [174]. The absorption peak present at 1270 cm^{-1} is identified as an exclusive β-phase peak [175]. Other prominent absorption peaks present are at 512, 839 1170 and 1400 cm^{-1} are also assigned to β- crystalline phase but not so conclusively because peaks due to γ- crystalline phase overlaps there [175]. Additionally, strong peak at 878 cm^{-1} is observed, which is feature of α- phase of PVDF as proposed previously from XRD pattern. Filler inclusion into the host polymer also flourishes crystallinity of the composites evident from sharpening of the absorption peaks.

4.3.2. FTIR analysis of PVDF/GO with varying GO concentration

IR Absorption spectrum of GO filled PVDF composite with varying GO amount in the wavenumber range of 400 – 4000 cm^{-1} is shown in fig. 4.5. Typical absorption bands of PVDF are present here ensuring their formation in β – crystalline form. After GO inclusion, all of those typical PVDF abortion bands are still present which verifies that they have gone through no structural deformation rather ensures formation of composite. First prominent peak observed at 480 cm^{-1} is an indication of formation of PVDF in either β or γ crystalline form. Although it may also represent α - phase, but since intensity of α – phase is relatively weaker in comparison, it is assigned to other two phases. There is also another peak observed at 510 cm^{-1} which is an exclusive β – phase peak. Sharp absorption peaks observed at 840 and 885 cm^{-1} corresponding to H – C – H rocking and F – C – F asymmetric stretching mode respectively in PVDF [170]. At 975 cm^{-1} another peak is present which is assumed to be the characteristic feature of α – phase present there at a very small amount also evident from XRD pattern. There are some other prominent peaks observed at 1072, 1170 and 1425 cm^{-1} represents C – C asymmetric stretching, F – C - F symmetric stretching and H – C – H wagging mode respectively [172]. The peak present at 1276 cm^{-1}

represents an exclusive β – phase peak while peak present at 1235 cm^{-1} corresponds to exclusive γ – phase [176]. Presence these peaks confirms formation of PVDF in β – phase dominant form. Apart from this, other peaks observed at 1072, 1232, 1375, 1470 cm^{-1} ensure presence of GO in those composites [177-178]. Thus FTIR absorption spectrum not only confirms formation of PVDF in β – phase but also ensures presence of GO there as nanofiller in the composite.

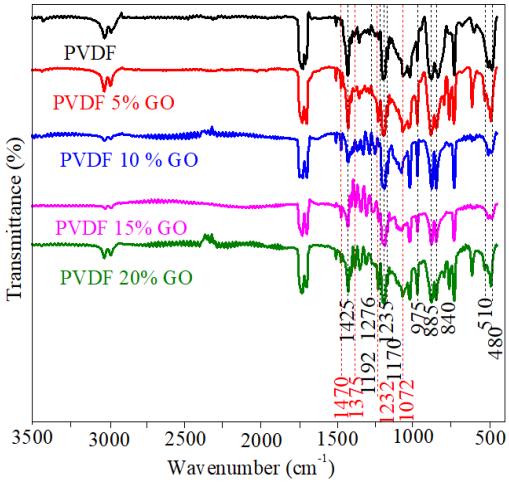


Fig. 4.5 FTIR spectrum of PVDF/GO composite films with varying GO concentration

4.4. X-ray photoelectron spectroscopic (XPS) analysis

XPS data was obtained using Kratos Axis Ultra DLD spectrometers using monochromatic Al K_α radiation (hν = 1486.58 eV). Survey and spectra were collected at fixed analyzer pass energies of 160 eV and 20 eV respectively. Obtained XPS data is then fitted by software, CasaXPS (version 2.3.16 dev67). These peaks are then fitted by asymmetric Gaussian – Lorentzian function after linear background correction [179]. Finally, this spectrum is charge corrected on the binding energy scale using the position of the main C 1s component at 284.5 eV as a reference for graphitic carbon [180]. The XPS spectra and their corresponding high resolution (HR) portion for C_{1S} region for all those films are shown in fig. 4.6 (a) and 4.6 (b) respectively. From the survey spectra

obtained from XPS analysis, presence of C, F and O in PVDF and PVDF/GO and C, F, Zn and O in PVDF/ZnO and PVDF/ZnO/GO are confirmed. Different elements present in these composites in atomic percentage fraction are presented in Table – 4.1. From deconvolution of HR spectra of those composites, incorporation of ZnO and/or GO into PVDF host has become apparent from the change in hybridization of C atoms present there in PVDF. The peak present at 285.6 eV for pristine PVDF representing C - C (sp^3 - C) bond shifts slightly around ~ 284.5 eV for PVDF/ZnO, PVDF/GO and PVDF/ZnO/GO composites which represents presence of sp^2 – C bonds. Because presence of ZnO and/or GO converts most of the sp^3 hybridized C atoms in PVDF to sp^2 hybridization. This is due to formation of F-C-O and O-C-O bonding environments due O containing reinforcements like ZnO and/or GO. Although C - H bonds in PVDF are present at ~ 284.3 eV overlaps with C = C bond in composites at ~ 284.5 eV, cannot be distinguished, but the increase in full width at half maxima (FWHM) of peak corresponding to C = C compared to that of C – H bonds ensures modification in bonding environment due to various nanofiller incorporation. The disappearance of C – O bond present at ~ 293.5 eV in those composite previously present at PVDF is may be due to absorption of O content by ZnO and GO. Due to formation of F - C-O and O-C-O bonds, ZnO and GO acts as oxygen acceptors in those composites. H-C-H peak of PVDF is absent in other composite films may be due to oxidation of H atoms. In this type of composites, F atoms of PVDF is usually bonded with C of GO or Zn of ZnO while H atoms got bonded with O atoms. There is report which suggests that generally F atoms of PVDF are bonded with C atoms of reinforcing materials [181]. This claim is further supported by identification of F-C and F-C-Zn bonds in GO and ZnO containing composites as seen from fig 4.6 (b). From Table – 4.1, it is observed that presence GO has considerably reduced oxygen content in those composites hints towards oxidization of H atoms by O atoms from GO forming H_2O molecules that ultimately vaporizes during drying process. This fact is also defended by vanishing of H – C – H peaks in O containing composites. In this way compositing GO through PVDF helps GO to liberate more O containing groups making it more reduced. Studies have proven that better reduction of graphene oxide makes it further suitable for conducting and opto-electronic applications [182]. Hence we conclude that there is enough changes in bonding environment of PVDF ensuring reinforcement of nanomaterials.

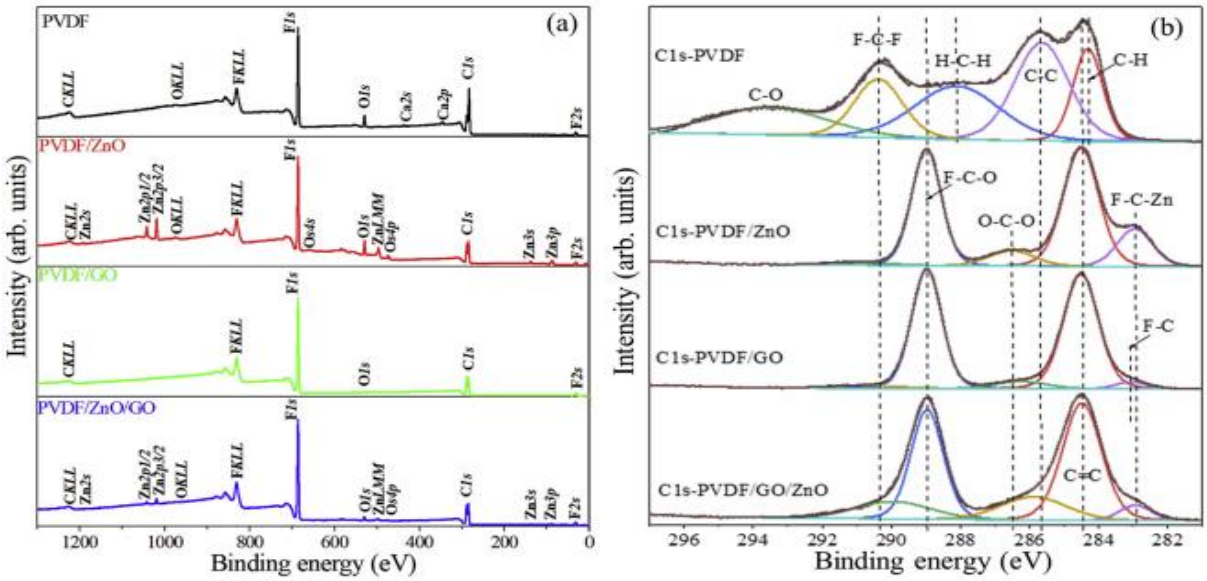


Fig. 4.6 (a) XPS spectra and (b) Deconvolution of C1s peaks of PVDF composite films

Table – 4.1 Different elements present in synthesized composites in atomic fraction obtained from XPS analysis

Film	C (%)	F (%)	O(%)	Zn(%)
GO	75.57	-	23.43	-
PVDF	65.19	29.11	5.70	-
PVDF/ZnO	53.80	37.91	6.09	2.20
PVDF/GO	54.23	45.26	0.50	-
PVDF/ZnO/GO	54.79	43.05	1.65	0.51