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Structural and physical studies of PVC/PVDF doped Nano lithium salt for electrochemical applications

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ABSTRACT

Polymer blend of poly (vinyl chloride) and poly(vinylidene fluoride) of nominal composition (30PVC/70PVDF) wt:wt was prepared in the form of thin films using casting technique. Samples of the same composition doped with gradient concentration of nano lithium salt (LTO) were prepared and studied. Proposed filler was characterized using Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), Transmission electron microscopy (TEM) and Electron diffraction (ED). Obtained data approve the crystalline nano structure of filler with a cubic structure of average size (25-30 nm). Prepared nano composites were then investigated using different spectroscopic methods. XRD reveals the amorphous nature of the base polymer blend with tendency for increase in crystallinity with increasing the content of lithium salt. FTIR shows a preservation of the main vibrational spectral bands in their position with small variation in the area and intensity of some spectral bands related to the interaction between polymer and filler.

Keywords:

PVDF/PVC; FTIR; Lithium ion batteries; XRD

1- INTRODUCTION

Recently, solid polymer electrolyte (SPE) has strained interest due to the wide application that involved in solid state including sensors and electrochemical devices. Some specified polymers mainly used as electrolytes in lithium batteries because it exhibits a high level of energy storage compared with their weight and size. Such electrolyte was prepared using high molecular weight polymer in combination with suitable alkaline salt and organic solvents [1-3].

Nowadays, lithium batteries replace the ordinary nickel-cadmium for and lead-acid batteries. Gel polymer electrolytes (GPE) including poly (methyl methacrylate) (PMMA) and poly (vinylidene fluoride) (PVDF) etc.. are considered as a superior and promising materials for high energy electrochemical devices. Many authors study complexation of PVC with PVDF [4], PS [5, 6].

PVDF is a semi-crystalline polymer that contain more than two crystalline forms. β-phase that encloses trans-planar (TT) chains responsible for piezoelectricity, while α-phase composed of random combination of trans-gauche isomers [7]. PVDF have a wide range of technological and biomedical applications in addition to uses in photo recording and microwave modulation due to their chemical resistance, high piezoelectricity, mechanical strength and process ability [8].

Polyvinyl chloride (PVC) is an amorphous linear thermoplastic polymer that have enormous industrial and commercial applications results from their unique properties and their accessibility to basic raw materials [9].

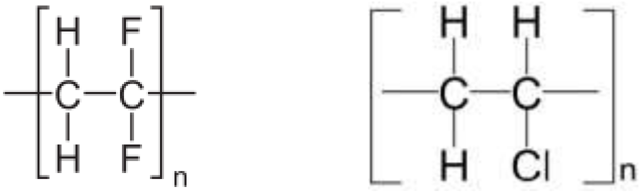
Power density and high energy are combination characterized Li ion batteries categorize them as unique technology for portable electronics that reduce green-house gas emission [10]. Lithium–metal alloys, e.g., lithium–tin alloys, or lithium salt alloy are among the most promising negative electrode materials to replace the conventional carbon-based compounds in advanced lithium ion batteries [11]. A promising anode material of high-rate lithium—ion batteries among the LTO phases is the spinal $Li_4Ti_5O_{12}$ and it was studied by several researchers in the lase decade [12].

Present work aims to introduce a new material based in polymeric matrices and containing lithium salt in the nano-scale suitable of lithium batteries application combined with investigation of the structural changes results for investigate structural and physical characteristic variations results from the process of preparation of nanocomposite and role of each constituent.

2. MATERIALS AND EXPERIMENTAL WORK

2.1. Materials

High molecular weight PVC and PVDF with average molecular weights 150,000 was supplied by Fluka and used as received without further purification. Lithium titanium oxide $Li_4Ti_5O_{12}$ (LTO) was purchased from Aldrich, USA, tetrahydrofuran (THF) was purchased from Fisher Chemicals UK. 70:30 weight/weight ratio of PVDF/PVC was dissolved in THF separately. Obtained solutions were then mixed and stirred vigorously and continuously together for 24 h until a clear homogenous liquid was achieved. Pre-determined concentrations of LTO were added to polymer blend and sonicated to about 3h to ensure uniform distribution of LTO. Obtained mixture was then poured into glass Petri dishes and kept at embient temperature to evaporate solvent. Dry films peeled from the glass dishes and stored in a vacuum dissector until use.



Scheme (1) Schematic representation for the chemical structure of pristine polymers

Table 1. Compositions and designations of PVDF-PVC-LTO

Designation	PVDF	PVC (wt.%)	LTO
S00	**70.0**	**30.0**	**0.00**
S02	**70.0**	**30.0**	**2.00**
S05	**70.0**	**30.0**	**5.00**
S10	**70.0**	**30.0**	**10.0**
S15	**70.0**	**30.0**	**15.0**
S20	**70.0**	**30.0**	**20.0**
S40	**70.0**	**30.0**	**40.0**

2.2. Methods

FTIR spectra were measured in the range 4000–400 cm^{-1} using Nicolet is10 single beam spectrometer to identify the main vibrational bands and the nature of complexation behavior between polymeric matrix constituents and that between polymeric matrix and filler. XRD spectra were recorded using PANalytical X'Pert PRO XRD system using Cu K_α radiation (where, λ= 1.540Å, the tube operated at 30 kV, the Bragg's angle (2θ) in the range of (5–70°).

The SEM micrographs of thin films were recorded using JXA-840 SEM (JEOL, Japan) to study the surface topography of the prepared films while TEM supported by electron diffraction was used to determine LTO filler size and to examine crystallinity of the filler.

3. Results and discussion

3.1. Characterization of LTO nanoparticles

FTIR Spectra of dopant LTO in the spectral range 4000-400 cm^{-1} were recorded using KBr tablet technique (100:1) KBr to sample in the form of transparent disk pressed in hydrolic press (5 ton/cm$^{2)}$. Figure (1) depicts the presence of characteristic broad absorption band centered around 3430 cm^{-1} attributed to stretching vibrations of the hydroxyl groups originating from Ti-OH. Additional observed peaks around 1750, 1735 cm^{-1} characterise stretch vibration of the C=O bonds in addition, $Li_4Ti_5O_{12}$ compound has a strong absorption peak at 686 cm^{-1} assigned to stretching vibrations of Ti-O bonds and TiO6 octahedron.

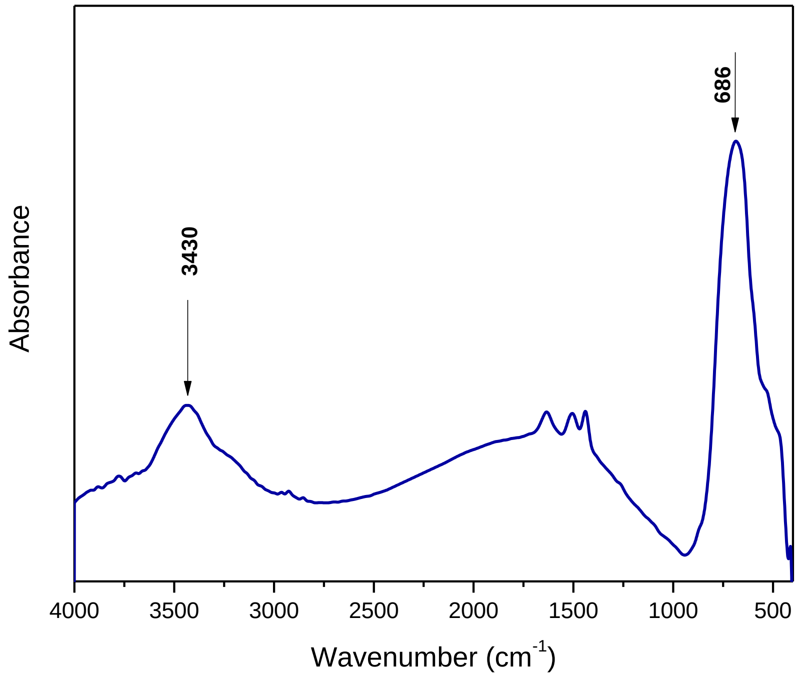


Figure (1) FTIR spectrum of $Li_4Ti_5O_{12}$.

Figure (2) reveals XRD pattern of crystalline LTO that characterized with sharp bands located at 18.5, 36, 44, 57, 66 and 79° assigned to (111), (311), (400), (511), (440), (531) and (444) planes. Claculated crystallite size was found to be ranged (20-30 nm).

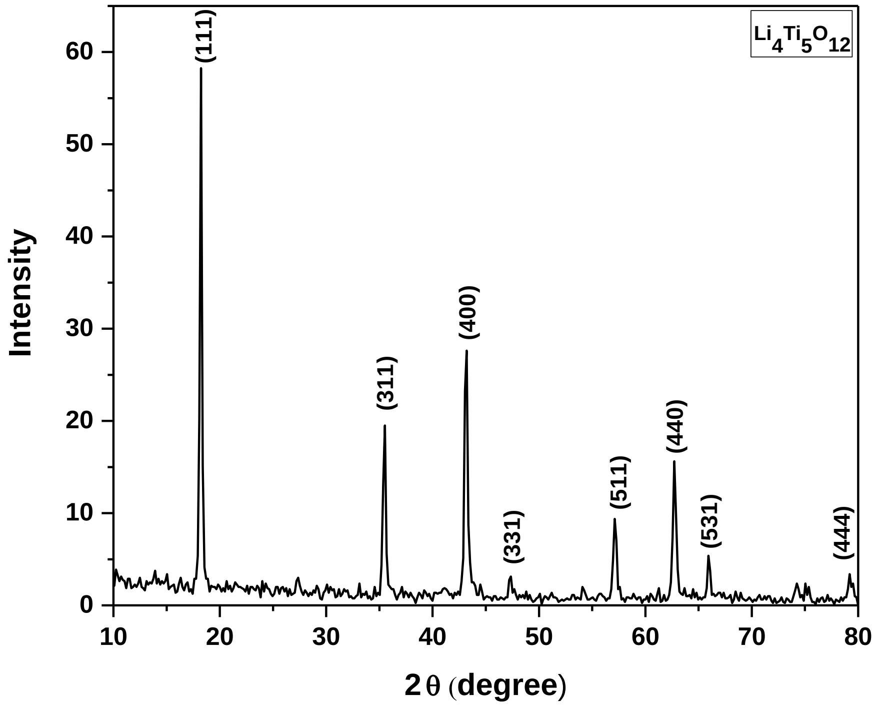


Figure (2) XRD pattern of LTO dopant

Figure (3) depicts TEM image of LTO dopant accombined with their electron diffraction. TEM shows that used LTO dopant having a cube like structure with an average size ranged from 25-30 nm while their electron diffraction pattern (ED) approves the crystalline nature and supports data obtained fom XRD..

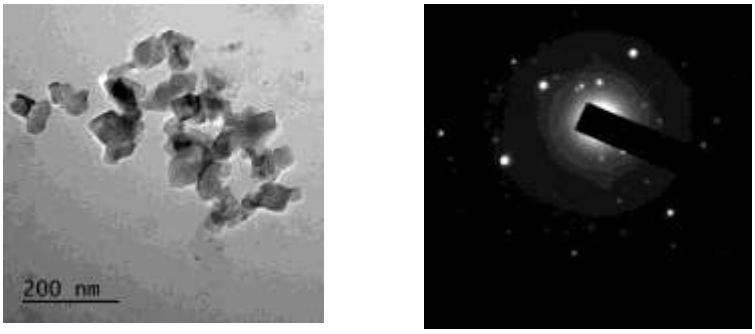


Figure (3) TEM Micrograph of LTO dopant combined with electron diffraction

3.2. Characterization of prepared nano-composites

3.2.1. X-ray diffraction

Figure (4) shows XRD pattern of pristine polymers and their blend films. X-ray patterns of pristine PVC polymer show the amorphous nature and characterize by two halos located at about 18.27 and 24.5° while XRD pattern of PVDF shows a semicrystalline nature with multiple peaks located at 18.30, 26.50, 33.10, 39.10° corresponding to (020, (022), (121) and (002) planes of α-phase and 19.7, 23.5, 36.5° assigned for (200), (210) and (101) planes of β-phase of PVDF. Spectrum of the 70/30 poly blend shows amorphous nature characterized by two halos point out to the complexation and miscibility of the two polymers as indicated by Abdelghany et al [13].

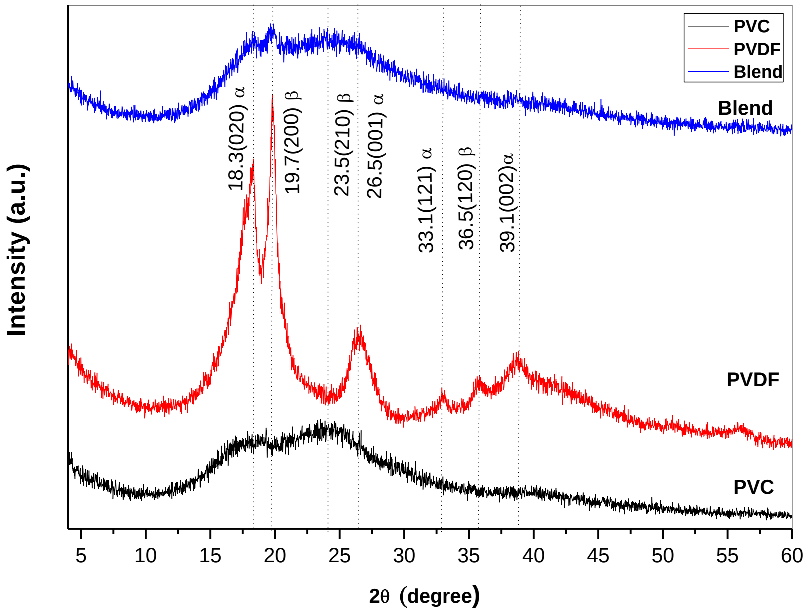


Figure (4) shows XRD pattern of pristine polymers and their blend films.

XRD of prepared nanocomposite contains increasing mass fractions of additional LTO are introduced in Figure (5). XRD pattern reveals a decrease in crystallinity as a consequence of LTO addition indicating complete dissolution, miscibility or gradient dispersion of LTO phase in the polymeric matrix phase that results also in a decrease of β-phase fraction F(β) which may be calculated from the following equation;

$$F(\beta) = \frac{A_\beta}{1.26\,A_\alpha + A_\beta} \times 100\%$$

Where A_α and A_β represent the relative areas corosponding to α and β phases shown and indexed in Figure (4) of PVDF is the sum of relative area corresponding to α and β phases respectively as reported by Abdelghany et al. [13].

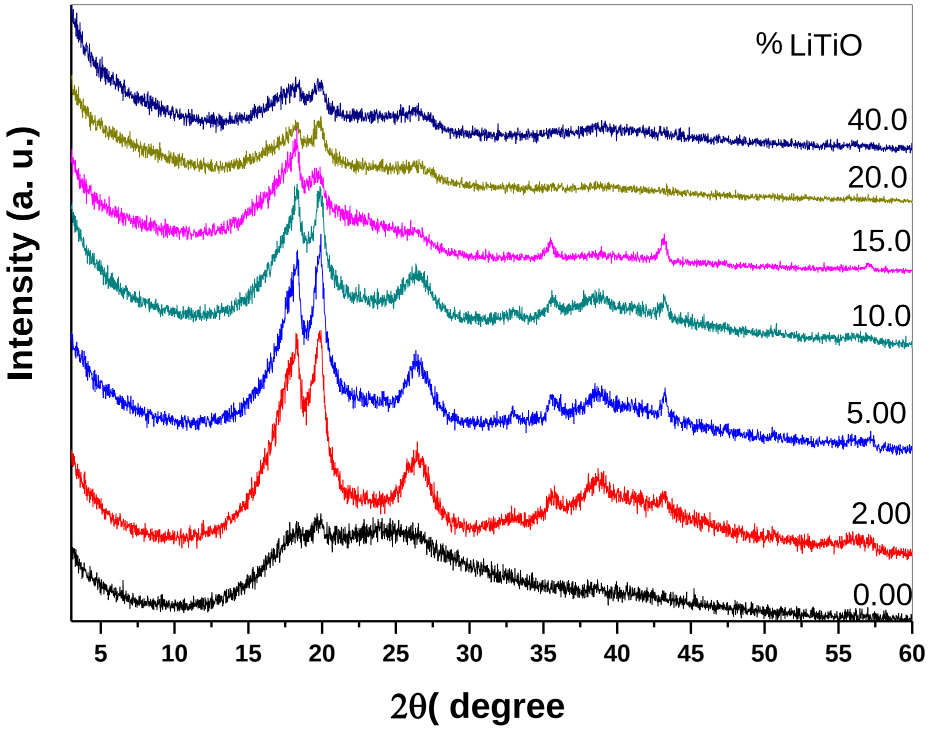


Figure (5) XRD of poly blend and samples that contains different amount of LTO dopant

β-phase fraction calculated values can be fitted with a quadratic equation with three degree of freedom and given by;

$$F(\beta) = 9.31 \times 10^{-5}\, x^2 - 0.01\, x + 0.25\ ,$$

where x is the dopant (LTO) weight fraction. Fitted data are shown in Figure (6) and listed in table (2).

Noticeable gradual change in the diffraction pattern of tested samples indicates not only a homogenous distribution of LTO dopant within the polymeric matrix but also indicate a complete dissolution of salt crystalline phase within the matrix without any evidence for aggregation or phase separation.

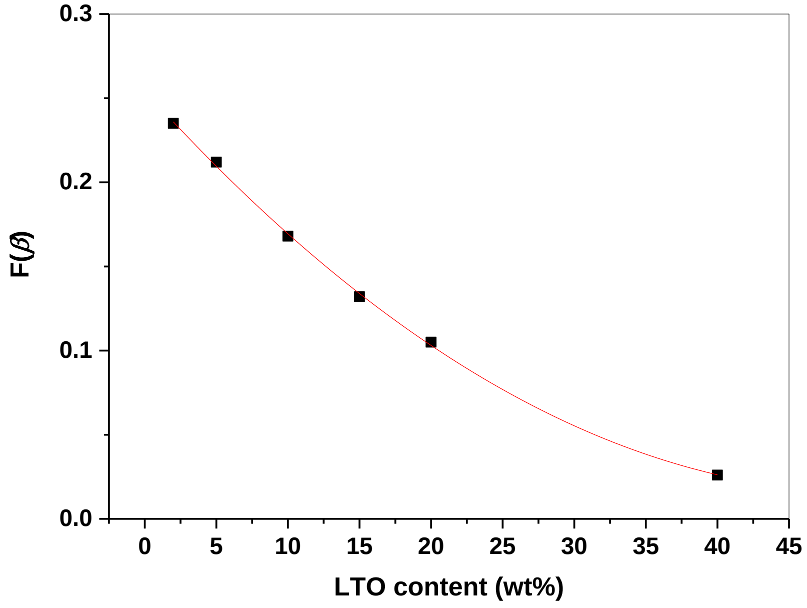


Figure (6) Change of β-phase fraction in relation to dopant content

Table 2 Calculated values of β-phase fraction

LTO Content wt%	F(β) %
2.00	0.235
5.00	0.212
10.0	0.168
15.0	0.132
20.0	0.105
40.0	0.026

3.2.2 FTIR absorption spectra

FTIR spectroscopy is a powerful nondestructive tool for structural investigation of prepared thin films of virgin and blended polymeric matrices. Figure (7) shows FTIR spectra of base constituent polymeric films combined with their blend films.

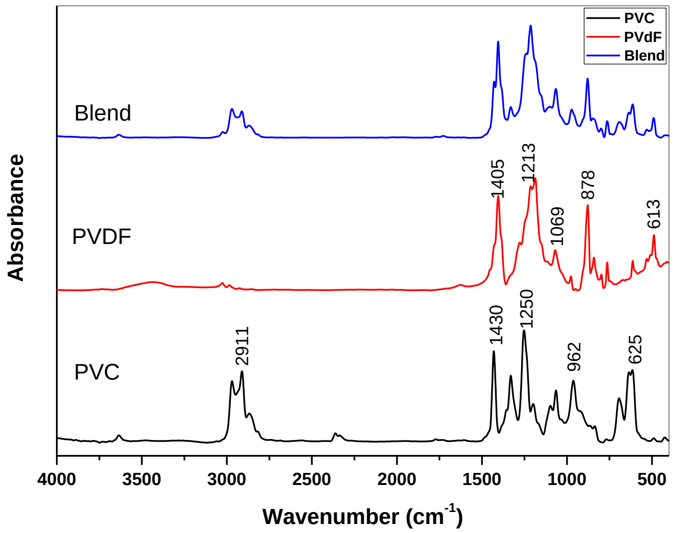


Figure (7) FTIR spectra of pristine polymers and their blend

FTIR spectra of PVC consists mainly of set of peaks in the spectral range 3000-2800 cm^{-1} attributed the C-H stretching vibrations (symmetric stretch at higher wavenumber and asymmetric stretching at lower one) followed by a peak around 1400 cm^{-1} due to aliphatic C-H bonding. The peak at about 1250 cm^{-1} assigned to the bending C-H vibration near Cl, C-C stretching bond vibration of the backbone chain structure located at 1100-1000 cm^{-1}. Finally, the vibration correspond to the C-Cl gauche bond was observed in the range 650-600 cm^{-1} [14]. Spectrum of PVDF includes C-H symmetrical stretching vibration observed in the range 3150 - 3030 cm^{-1}. A series of weak combination and overtone bands appears and the pattern of the overtone bands reflects the substitution pattern of the benzene ring in the spectral range 2000 –1670 cm^{-1} region. α-phase of PVDF is evidenced particularly by the peaks 435, 486, 603 and 768 cm^{-1}, while the β-phase is characterized by the peaks at 510 and 838 cm^{-1} [15]. The peak at 510 cm^{-1}, belonging to the β-phase, are assigned to CF_2 bending and wagging modes. The band at 836 cm^{-1} is assigned to CH_2 bending deformation, belonging to the β-phase [8].

Table (3) list the FTIR band position of constituent pristine polymer and in combination with their assignment previously discussed by different authors [8, 14, 15].

Table 3 FTIR band position and assignment of prepared samples

Sample	Wavenumber (cm^{-1})	Assignment
PVC	3000-2800	C-H stretching vibrations
	1400	aliphatic C-H bonding
	1250	bending C-H vibration near Cl
	1100-1000	C-C stretching bond vibration of the backbone chain structure

	650-600	C-Cl gauche bond
PVDF	3150-3030	C-H symmetrical stretching vibration
	2000-1670	weak combination and overtone bands
	435, 486, 603, 768	α-phase characteristic bands
	510, 838	β-phase characteristic bands

Figure (8) reveals FTIR absorption spectra for (PVDF/PVC) poly blend sample and other samples that contain variable amount of dopant (LTO) incorporated within the polymeric matrices. The presence of the low intensity broad band at about 1200-1300 cm^{-1} assigned to the hydrogen bonding between C-H groups from PVC to CF2 groups of PVDF. In addition, a noticeable change in band intensity and position in comparison of the base poly blend sample were observed especially, for the vibrational bands located at 849, 879 and 1405 cm^{-1} assigned for the high polarizable γ-phase of PVDF. Mentioned band observed to growth in intensity with increasing content of LTO. The change in bands shape and position of the peak around 1400 may be assigned to interaction, complexation and dissolution of the salt crystalline phase in polymeric matrices results from progressive addition of LTO [16].

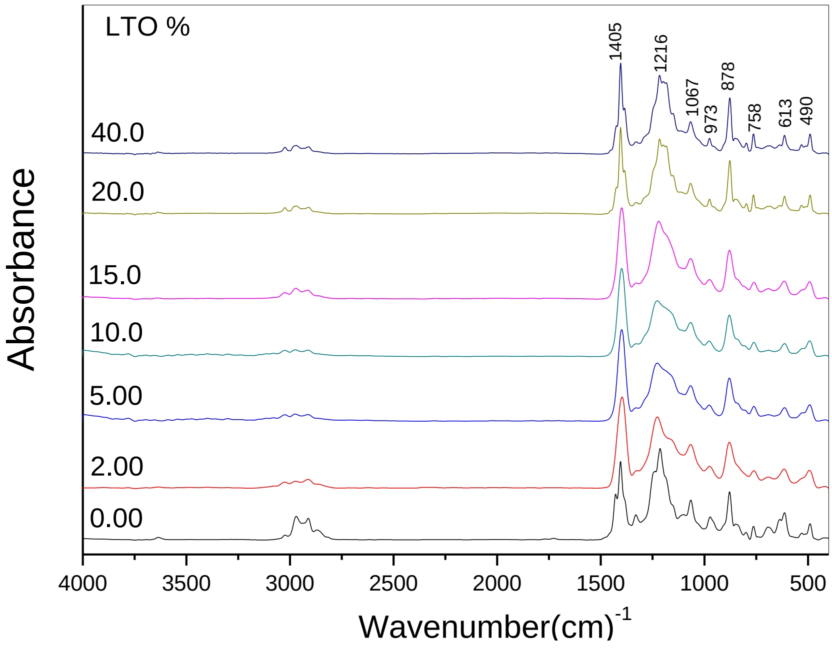


Figure (8) FTIR spectra of poly blend and samples that contains different amount of LTO dopant

Conclusions

Samples of PVDF/PVC polymer blend in addition to other samples that contain gradual increasing content of LTO salt up to 40 wt% were successfully prepared. FTIR of dopant materials shows the presence of characteristic broad band due to hydroxyl groups (Ti-OH) in addition strong band at 668 cm^{-1} origininating from Ti-O bonds and TiO6 octahedron. XRD approve the crystalline nature of used dopant and calculated value of crystallite size was found to be ranged (25-30 nm) and in agreement with data obtained from TEM and electron diffraction.

XRD of prepared nanocomposite reveals a decrease in crystallinity indicating complete dissolution, miscibility or gradient dispersion of LTO phase in the polymeric matrix phase without any evidence for aggregation or phase separation combined with a decrease of β-phase fraction F(β) fitted to a quadratic equation with three degree of freedom.

Low intensity FTIR absorption band at 1200-1300 cm^{-1} assigned to hydrogen bonding between C-H groups from PVC to CF2 groups of PVDF. The change in bands shape and position of the peak around 1400 was attributes to the interaction, complexation and dissolution of the salt crystalline phase in polymeric matrices results from progressive addition of LTO.

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