Chapter 3

LITERATURE REVIEW AND SYNTHESIS: CNT AND ZnO DOPED EAP

From literature survey, it is studied that there are different type of materials related to Electro-active Polymer (EAP) and these functional materials have unique academic and technological application in future. In our research work, we consider LCEs and Polyaniline type electroactive polymer with CNT and ZnO as dopant. A brief review on synthesis work and various properties of these Electro-active Polymers is in the following section.

3.1 Liquid Crystal Elastomer (LCE)

Liquid crystals are typical fluids with rod like molecules having long range orientation order. The simplest ordering is the nematic order where mean ordering direction is uniform about the director. Liquid crystals can be oriented by the application of electric field due to presence of both anisotropy and fluidity. These molecules expand when their component rods orient. A change of shape thus takes place but earlier the effect was very less. Now it is observed that linking the polymer chains together into a gel network fixes their topology and the melt becomes an elastic solid-a rubber. These materials are known as liquid crystals elastomers (LCE), discovered very recently and due their large flexibility, less response time are becoming the subject of hot research.

Many researcher works synthesis and characterization of these smart and active materials. Finkelmann et al. [1] synthesized LCE carrying mesogenic molecules as side chains to the main chain. The dramatic mechanical properties of side-chain liquid-crystalline polymers based on siloxane backbones are due to a much higher chain anisotropy and are conveniently liquid crystalline at room temperature. They also report that method of cross linking have varied from chemical using copolymerization with a small proportion of reactive groups. Finkelmann also synthesised nematic single LCE by
using swelling experiment & measured mechanical and order parameter by Nicolet FTIR spectrometer using linear polarizers. The whole experiment is carried out under equilibrium condition [2]. This group also studied mechanical properties of monodomain side chain nematic elastomers and found that the relaxation time is slowest relaxation time of network (as whole) which are consistent with hydrodynamics description of nematic elastomer. In recent years, they introduced a new synthesis concept for LC-elastomers having the liquid crystalline units in the main chain as well as in the side chain. The main chain LC polymer used as cross linker is a LC-polyether which was previously synthesized. These new LC-coelastomers show spontaneous change in length at the nematic to isotropic phase transformation temperature up to 300%. This in dielectric elastomers (such as silicones) is found up to 30-40%. Also, Cornell group has prepared lightly cross-linked (i.e. rubbery without swelling) nematic and smectic elastomers based on the rod-like mesogenic monomers connected via flexible spacers [3].

Sung et al. [4] synthesized liquid single crystal elastomer by using anisotropic deswelling method. They found anisotropic deswelling of a partly crosslinked network causes an oblate network chain conformation that is sufficient to cause a macroscopic orientation of the cholesteric phase structure. This state of orientation is locked by a proceeding crosslinking reaction. They suggest that the spontaneous changes of dimensions at isotropic-to-cholesteric phase transformation are due to overall oblate chain conformation of the final network and this shows interesting opto-mechanical properties. Another group Antoni also synthesized cross-linked smectic-C main chain liquid-crystalline elastomer via polycondensation process. They studied and analyzed different deformation processes on a conical layer distribution structure of SmC main chain liquid-crystalline elastomer in detail. They applied stress-strain and X-ray experiments to identify and confirm structural modifications during deformation [5]. They found that uniaxial deformation of the elastomer parallel to the director causes an increase of the tilt angle without affecting the director orientation which is accompanied by an increase of the Young modulus parallel to the director. The reorientation process also affects tilt angle of the smectic structure and observed after complete reorientation a tilt angle is corresponds to the tilt angle of the sample under uniaxial strain parallel to the director. They also found that basic difference between main and side-chain elastomers is in main-chain elastomers
the mechanical field always couples to the tilt angle of the SmC phase structure. This opens
new interesting aspects especially for chiral SmC* elastomers, where the tilt angle are used
to determines and explore the optical as well as ferro-electrical properties.

Tajbakhsh et al. [6] report the systematic study of uniaxial monodomain nematic
elastomer. They found that results obtained are sensitive function of concentration of main
chain component and these pronounced slowing down of all response process i.e stress
relaxation, euillibration of natural length as well as shape recovery. In same year, Terentjev
studied a wide range of photo sensitive materials based on azobenzene molecular moieties
and found that differing composition & topologies are reflected in varied mechanical
response to radiation with ultraviolet light [7].

Gleim et al. [8] studied the measurements of stress and birefringence of cross
linked liquid-crystalline side chain polymer and obtained results are compared with those
obtained for conventional elastomers. They found that thermo-elastic behaviour in the
nematic state completely differs from that observed for common polymer networks due to
the anisotropic ordering of mesogenic side chains. They also studied photo-elastic behavior
and prove proportionality of stress and birefringence above the clearing temperature T,
which is similar to common elastomers. They found that stress-optical coefficient;
however, strongly correspond on temperature in the pre transformation region. X-ray
measurements show a uniform orientation of the mesogenic side groups in the nematic
state and diffraction patterns observed contain many more reflexes than observed for
common nematics one. Dannio et al. also studied thermotropic and elastic properties of
main chain LCE by monomer and crosslinker molecular control. They found that choice of
cross linker can be made according to behaviour expected for materials i.e mechanical
resistant materials or very elastic / high strain capable materials [9].

Joachim et al. [10] reported that the state of order of nematic elastomers can be
considerably influenced by the elastic deformation via polymer network. The magnitude of
effects is significantly higher than the comparable effects in electric or magnetic fields.
While the nematic-to-isotropic phase transformation, temperature is clearly shifted by the
mechanical stress towards higher temperature for the elastomer investigated and a critical
point is not observed due to poor mechanical properties. They also calculate the
coefficients of the Landau free energy expansion with experimental data to determine all
critical value. They also suggest that with an increasing cross linking density and a decreasing spacer length should improve the liquid crystal network interaction and a critical point should be directly observed in the mechanical field.

Donald et al. [11] studied free-standing anisotropic side chain liquid crystalline elastomer films prepared using mesogens with laterally affixed polymerizable side chains. They presented data on two networks: one containing the monomer of 4-acryloyloxybutyl 2,5-(4-butyloxybenzoyloxy) benzoate and another from a 50/50 mol % mixture of the above with 4-acryloyloxybutyl 2,5-di(4-pentylcyclohexyloxy) benzoate and showed phase transition to be 30 to 45%. The order parameters of the oriented films were determined from the dichroic ratio of IR absorption at 3343 cm\(^{-1}\) to the inplane aromatic stretching overtone of the LC mesogen core. This showed that the variation of the order parameter with temperature scales similar to the strain changes at constant stress. Isostrain studies, conducted through the nematic to isotropic phase transition, shows that the two networks behave as true elastomers with significant differences in the force developed.

Liu et al. [12] developed a new kind of muscle-like material based on a network of side-on nematic LC homopolymers. They used side-on LC polymers instead of main-chain LC polymers for synthetic reasons. These materials were thermoresponsive, with a typical contraction of around 35–45% and a generated force of around 210 kPa. Subsequently, a photo-responsive material was developed, with a fast photochemically induced contraction of around 20%, triggered by UV light. They also prepared micrometre-sized artificial muscles. Cladis studied Liquid crystalline elastomers (LCEs) composed of low molecular weight mesogenic units tethered to a cross-linked polymer network [13]. They have shown that due to remarkable shape changing properties in LCE at the nematic-isotropic phase transition that could serve as generic large amplitude, low frequency actuators and sensors i.e. artificial muscles.

David et al. [14] showed that fibrillar collagens and the dragline silk of web spiders belong to this remarkable class of materials. The identification of these biopolymers as LCEs may have a predictive value. It may explain how collagens and spider dragline silks are assembled. It may provide a detailed explanation for their mechanical properties, accounting for the variation between different members of the collagen family and between the draglines in different spider species. It may provide a basis for the design of biomimetic
collagen and dragline silk analogues by genetic engineering, peptide or classical polymer synthesis. Biological LCE may exhibit a range of exotic properties already identified in other members of this remarkable class of materials. R. Zentel *et al.* developed micrometer-sized actuators by heatable micro-fluidic setup to prepare monodisperse, spherical particles from liquid crystalline elastomers and able to control their size by using experimental parameters between 280 to 550 μm. They found that when the particles are heated into the isotropic phase of the liquid crystal that shows a strong and reversible shape change to a cigar-like conformation where the length of one axis is increased by up to 70% [15]. They argue that the actuation properties of these particles are the result of uniform concentric alignment of the mesogens.

Terentjev *et al.* [16] reported a significant electromechanical response in nematic liquid crystalline elastomers filled with a very low 0.01% concentration of carbon nanotubes, aligned along the nematic director at preparation. They show that nanotubes create a very large effective dielectric anisotropy of the composite; their local field-induced torque is transmitted to the rubber elastic network and is registered as the exerted uniaxial stress of order 1 kPa in response to a constant field of order 1 MV/m. They also found that dependence of the effect on field strength, nanotube concentration and reproducibility under multiple field-on and off cycles. The results indicate the potential of the nanotube-nematic elastomer composites as electrically driven actuators. Muhoray also studied that light can change the orientation of liquid crystal molecules and torque that causes reorientation originates in angular momentum transfer from radiation field to the materials. If a small amount of dichroic dye is dissolved in liquid crystal, a light induced torque can appear essentially without the transfer of angular momentum from light [17]. They show that in such cases, the dye molecules act as light driven molecular motors via an orientational Brownian ratchlet mechanism, transfer angular momentum, which originates at the cell walls to the liquid crystal. The detail of this mechanism shows important applications ranging from flat-panel displays to opto-mechanical transducers [18].

### 3.1.1 Synthesis of LCE

In 1981, Finkelmann group from Freiburg University synthesized the first LC elastomers [2]. After that some groups synthesizes different LC elastomer by using different cross
linking agent with polymer backbone and liquid crystal monomers (commercially available) [19-20]. In our research work LCEs are synthesized in our laboratory by following method [21] (scheme given in Figure 3.1).

![Scheme for synthesis of Nematic LCE](image)

Figure 3.1: Scheme for synthesis of Nematic LCE [2].

Polydomain, aligned samples were made by preparing partially crosslinked films in a centrifuge, highly swollen in toluene (2-3 ml per 1 g of material), reacting for 25-35 minutes before evaporating the solvent. A careful study of reaction kinetics ensured that approximately 50% of crosslinks were established in the first stage of this preparation. The orientation is then fixed by the subsequent second-stage reaction, when the remaining crosslinks are fully established. The better alignment contrast to the crosslinking is obtained in a stretched polydomain nematic phase [22-23]. The synthesized LCE phase identified as nematic one by analyzing polarized optical microscope as well as FTIR Spectroscopy.

### 3.1.2 FTIR Characterization of Nematic LCE

Evidence of NLCE synthesis was obtained by FTIR spectroscopy. According to FTIR spectra, spectral peak obtained at 3445 cm\(^{-1}\) was due to some moisture in the sample.
(water), peaks in between 3445 and 2926 cm\(^{-1}\) was due to benzene C-H bond, peaks at 2926 and 2857 cm\(^{-1}\) was due to long chain of -CH\(_2\)- group respectively, peak at 1731 cm\(^{-1}\) was due to C=O group, peak at 1606 cm\(^{-1}\) was due to C=C group, peak 1509 cm\(^{-1}\) due to benzene (C=C), peak at 1465 cm\(^{-1}\) was C-H deforming ,1256 cm\(^{-1}\) was Si-C bond, 1196 cm\(^{-1}\) was due to C-O (simple present in the group), 1069 cm\(^{-1}\) was due to C-O of benzene group, 1009 cm\(^{-1}\) was Si-O bonding, 763 also confirms benzene in the sample. The obtained peaks value were similar as in literature and confirm the synthesis of polydomain NLCE [as shown in Figure 3.2].

![FTIR spectrum for Nematic LCE.](image)

**Figure 3.2: FTIR spectrum for Nematic LCE.**

### 3.1.3 Optical Polarizing Microscopy

In order to carry out phase identification studies and to know the phase transition temperatures, we used Dewinter polarizing microscope and custom built temperature programmer cum hot stage mounted on the polarizing microscope stage. The textures were captured on the computer interfaced with the polarizing microscope through a CCD camera. All the optical textures have been investigated under crossed polarizers at 40X.
our research work, we carried out detailed micro textural investigations of NLCEs at different temperature.

3.1.3 Experimental set up

To identify the phase transition of LCE Dewinter polarizing microscope is used with hot plate. A complete set up to identify phase is given in Figure 3.3 below.

![Experimental Setup Diagram]

Figure 3.3: A schematic representation of Image analysis
Optical polarizing microscope (OPM) is the most widely used technique to identify different phases. The synthesized material of NLCE under investigation is studied at crossed polarized light for various temperatures of heating and cooling cycles. The textures obtained by OPM are shown in Plate 3.1. In these textures molecular alignment and defects are seen at different temperatures. It is found that the NLCE material possesses nematic phase upto a temperature of 76°C followed by isotropic phase.
Plate 3.1: Different NLCE textures at different temperature and near isotropic phase at 80°C.
3.2 Pure and MWCNT doped Polyaniline Nanocomposites

Among different conducting polymers polyaniline consider a very important class of electronic/conducting polymers. Polyaniline (PANI) exists in different forms which differ in chemical and physical properties and depending on method of preparation, polyaniline bases may exist in a fully reduced form (leucoemeraldine), partially reduced form (emeraldine), and fully oxidized form (pernigraniline) [discuss in Chapter 1, section 1.3.2].

![Chemical structure of Polyaniline](image)

Figure 3.4: Chemical structure of Polyaniline

In order to synthesis pure PANI and CNT doped PANI composites, many efforts have been made to combine PANI and CNT in producing composite materials with improved properties which are enable to be used in different applications. A detail inspection of literature regarding synthesis, characterizations and different properties devoted to composite based on PANI (as host) and MWCNT (as guest) are given below:

First, PANI/MWCNT composites were prepared in 1999 [23] and since then have been the subject of intensive research and considerable progress has been made in their synthesis procedure. The composites include PANI/MWCNT prepared via chemical oxidation of aniline in acidic aqueous environments with an oxidizing agent like ammonium persulfate, which exhibit site-selective interactions between the quinoid ring of the repeating units of PANI emeraldine salt and MWCNT [24], a coaxial nanowire of a PANI/MWNT composite prepared by electrochemical oxidation of aniline on a MWCNT electrode [25], and a PANI/MWNT composite with high electrocatalytic activity for formic acid oxidation, synthesized by microemulsion polymerization of aniline in the presence of MWCNT [26-27].

Luo et al. [28] studied the inclusion CNTs in a PANI–HRP (horseradish peroxidase) biosensor system and significant change in performance of the resulting
biosensor is obtained. In this biosensor system, CNT play two important roles, one is as a type of nanomaterial, which can effectively adsorb enzyme and thus increase the amount of immobilized enzyme to enhance the stability of the biosensor. Another one is the doping of PANI film with CNT can greatly enhance the conductivity of the resulting film and increase the electron transfer efficiency. The PANI/CNT/HRP biosensor responded to $\text{H}_2\text{O}_2$ very rapidly with good sensitivity and could be suitable for interference-free detection of $\text{H}_2\text{O}_2$.

Soundararajah et al. [29] investigating the improved mechanical property of polyaniline (PANI) intercalated with montmorillonite (MMT) clay. The MMT–PANI nanocomposites displayed improved mechanical properties compared to the neat polymer or clay. The obtained results shows the mechanical properties of the MMT–PANI nanocomposite, Young’s modulus, fracture toughness, hardness and impact energy of polyaniline significantly increased by the presence of MMT clay in the nanocomposite of PANI and MMT up to 23 wt.% of MMT and decreased at higher clay contents. The degree of exfoliation and the bond strength of the MMT clay attribute to the better mechanical properties.

Sharma et al. [30] synthesized films of polyaniline (PANI) and polyaniline/CNT composites via solution casting technique. The PANI and PANI/CNT composite film studied and confirm interaction between CNT and the molecular chains of PANI by FTIR spectroscopy. These films have also been used to investigate the dielectric properties in range of 8.0–12.0 GHz of frequency. The higher value of dielectric constant of PANI/CNT composite films can be described to the interaction of PANI molecular chains with the CNT surface. The loss factor of these composite films also increases and expected due to because of incorporation of CNT in PANI matrix, hence increases in its conductivity.

Keivani et al. [31] prepared Polyaniline (PANI) in the presence of bronsted acid from aqueous solutions chemically. Polyaniline-nylon-6 composite (termed as PANI/Ny6) prepared via solvent casting technique. The preparation conditions of the polymer composite were optimized with regard to mechanical properties and found that to determine mechanical properties of polymer composite have greatly effect the molar ratio of PANI to nylon. It is also observed that electrical conductivity is decreased with increasing of nylon percentage in polymer composite.
Ramamurthy et al. [32] fabricated high molecular weight polyaniline / multi-walled carbon nanotube composite films using solution processing. Composite films with various weight percentages of multiwalled carbon nanotubes were fabricated. Physical properties of these composites were analyzed by thermogravimetric analysis, tensile testing, and scanning electron microscopy. These results indicate that the addition of multiwalled nanotubes to polyaniline significantly enhances the mechanical properties of the films. In addition, metal–semiconductor (composite) (MS) contact devices were fabricated, and it was also observed that the current level in the films increased with increasing multiwalled nanotube content. Furthermore, from these result, the optimal concentration of MWNTs appears to be about 1%; however, further investigation will be required to determine a more precise optimal composition. Thus, the optimized PANI/MWNT composite has the potential to produce organic electronic devices with much more current drive than pure PANI, leading to many useful applications in optoelectronics.

Upadhyay et al. [33] reported synthesis, characterization, thermal degradation as well as stability of polyaniline (PANI) and their substituent polymer. Their different physical properties were studied and compared with pure PANI, to find out effect of electron donating groups (—CH₃) and electron withdrawing groups (—Cl, —NO₂). Author also found that presence of any type of substitution in benzene ring of aniline increased the solubility but consequently reduce the yield, thermal stability as well as electrical conductivity. FTIR and UV-Vis spectroscopic technique were used to characterizing structural change in these polymers. Also, TGA were used to explain thermal degradation and stability of these polymers and conductivity measurements. These studies reveal and conclude that PANI shows maximum thermal stability among other polymers and order of thermal stability is given via PANI > POMA > PMNA > PMCLA.

Tahhan et al. [34] reported that addition of PANI by simply coating of CNT material substantially which enhance actuation strain of the original CNT and found that actuation dominated by the PANI redox processes, although CNT provided a reinforcing effect that allowed high strains to be maintained at high applied stresses. Similarly, nanotubes increased conductivity of the nanocomposite (−10 to 14 mA) than that in PANI (−2 to 3 mA) and CNT (−5 to 4 mA) at a same physical condition and applied voltage, which results to improve electrochemical efficiencies. Optimization of CNT/PANI
nanocomposites using different fabrication methods, to achieve a high actuation strain contributed by PANI component and high Young’s modulus (40–100 GPa) by CNT component would lead to a high actuation work-per-cycle.

Khalkhali et al. [35] has explore polyaniline conducting polymer (PANI) as application in a sensor material for detection of some agricultural organophosphorus compounds like dichlorvos, trichlorophon, and chlorpyrifos that are commonly used as insecticides and pesticides. They also investigated the effects of concentration, thickness of the polymer film etc on some important measurements such as electrical conductivity and stability for these compounds. It was also found that adsorption and desorption of these compounds on PANI film which cause measurable change in resistance of conducting polymers.

Mahulikar et al. reported the comparative study of corrosion protection performance of the coatings containing nanopolyaniline and polyaniline/TiO₂ nanocomposites on carbon steel in epoxy binder [36]. The PANI was prepared via emulsion polymerization method of aniline using ammonium persulphate. These synthesized polymers were characterized by FTIR, XRD, SEM and TEM techniques to determine structural, particle size and surface morphology modification. The corrosion protection performance of the coatings was evaluated by using weight loss measurement in different corrosive media for 960h. Furthermore, immersion test was carried out in an aqueous solution of NaCl for 720h and corrosion of the panels was monitored by visual inspection. The water adsorption in the prepared coatings was also studied and observed that the PANI/TiO₂ in epoxy coating showed better physico-mechanical properties as compared to nano-PANI containing coatings. Therefore, these study concludes the PANI/TiO₂ nanocomposites could be useful as an excellent adhesion promoter and corrosion inhibitor.

Sridevi et al. studied the influence of dopant on conductive polymers and shows dopant plays an important role to convert the polymer form into conductive network form [37]. This shows that conductivity of a polymer can be increased several-fold by doping process if suitable dopant is used as dopant. The synthesize polyaniline chemically with various types of dopant acids, which act as an oxidative agent as well as a secondary dopant resulting in a Polyaniline/Gold nanocomposite. The impact of content of dopant
acids during polymerization of aniline was also studied. The different techniques like UV-Vis Spectroscopy and FTIR spectra were used to determine level of doping, nature of the polymer and the incorporation of Au seems to be effective for better conductivity of the polymer samples respectively. Also, XRD study used to confirms the presence of Au nanoparticle in the polymer matrix in nanometer scale.

Doyeon et al. measured the electrical conductivity of the PANI/CNT composite thin film in response to near infrared, as a bolometric sensor resulting in a sensitivity enhancement of more than two orders of magnitude compared to polyaniline or CNTs. They also suggests that the effective enhancement in sensitivity is due to the synergistic effect, where the PANI/CNT composite thin film benefits from both the higher heat generation of CNTs and the higher temperature coefficient of resistivity of polyaniline [38].

Nagaraja et al. synthesized PANI and PANI/CNT composites by using an oxidative chemical polymerization method below room temperature and found that aniline molecules were initially adsorbed then polymerized on the surface of CNT. The FTIR spectra were used confirm the presence of PANI in the composite and this spectrum reveals that there was some interaction exists between the PANI and CNT [39]. They also used SEM and XRD spectrum to confirm that CNT embedding in the PANI matrix and PANI wrapped completely on the surface of the CNT. The electrical conductivity of PANI/CNT composites ewas found higher values than pure PANI (maximum conductivity obtained 4.44 S/cm at 20 wt % of CNT) and this increase in conductivity of the composite linear with increasing CNT concentration.

From literature survey, it is found that efficient polymerization of aniline is done only in an acidic medium effectively, where aniline exists as an anilinium cation. A variety of organic and inorganic acids with different concentration have been used in the synthesis of PANI and resulting PANI protonated with various acids, differs in solubility, conductivity and stability. In our research work, we have selected hydrochloric acid in equimolar proportion to aniline i.e. aniline hydrochloride is used as a monomer for synthesis. The handling of solid aniline salt is preferred to liquid aniline because of the point of view of toxic hazards. Peroxydisulfate is the most commonly used oxidant and its
ammonium salt was preferred to the potassium counter part because it is good soluble in water.

There are different methods by which PANI/CNT polymers composites can be synthesized, depending on the desired applications. PANI/CNT polymers composites can be synthesized in presence of different protonic acid media by different methods. The most widely accepted methods are chemical oxidative polymerization method and electrochemical methods. Chemical oxidative method is preferred over electrochemical polymerization because of its cost effectiveness and bulk quantity of the polymer that can be prepared during the onset of a reaction.

3.2.1 Materials Required

In order to synthesis pure and MWCNT nanocomposites, AR grade Aniline (99%) and Ammonium persulphate (APS) (99%) are purchased from Sigma Aldrich (used as received). Other supplement chemicals are of AR grade and used as received. All the aqueous solutions were prepared using double distilled water. The MWCNT used are synthesized at National Physics Laboratory by a chemical vapour deposition method. The diameter of the synthesized MWCNT range from 30−50 nm with a typical length ranging from 0.3 μm to several μm.

3.3 Synthesis of PANI Polymers

The chemical oxidative polymerization of aniline is carried out as report in [31]. At the start of the reaction, 0.1 mol/L aniline are dissolved in 1 mol/L HCL solution. Polymerization reaction is started by drop wise addition of aqueous solution of Ammonium persulphate (APS) and the reaction is carried out for 8 h at 0°C-5°C temperature with contineous constant stirring. The reaction mixture is then kept over a whole night at room temperature, after which the formed polymer precipitates are filtered, then washed several times with distilled water thoroughly until filtrate become colourless, followed by methanol in order to remove low molecular weight oligomers like ammonia [40]. Finally, the resultant precipitate is dried in oven for 5 hour to achieve a constant weight and then pressed to form powder. The ratio of monomer to oxidant is taken 1:1, because we found
that with this ratio the productivity and conductivity of the resultant polymer are very good. Polymerization reaction of aniline is generally carried out for 2–6 h, but the productivity of polyaniline composites even after 5 h was very low. So, the polymerization time 8 h is set to produce all the polymers.

3.3.1 FTIR Spectra for Pure PANI

Figure 3.5 represents the FTIR spectrum for synthesized pure PANI

![FTIR Spectrum for pure PANI](image)

Figure 3.5: FTIR Spectrum for pure PANI

FTIR spectra were measured by Perkin Elmer spectrometer using the KBr pallets technique. For structural characterization FTIR is an important physical tool. FTIR spectrum of a chemically synthesized polyaniline is shown in Figure 3.5 shows vibration bands at 3425, 2981.88, 1486.31, 1292.90, 1112.68 and 793.45 cm\(^{-1}\) etc. These values represent the characteristic peaks of polyaniline chain and in agreement with theoretical one [31]. The 3425 cm\(^{-1}\) vibration band has been attributed to the stretching vibration of secondary amine. The vibration band seen around 2981 cm\(^{-1}\) has been ascribing to aromatic
C-H vibration. The peaks at 1600 cm\(^{-1}\) vibration band is due to the C = C double bond of quinoid rings, whereas 1486.32 cm\(^{-1}\) vibration band arises due to vibration of C = C double bond which associated with the benzenoid ring. Similarly peak at 1500 cm\(^{-1}\) may be due to strong symmetrical bending band and it may be due to secondary aromatic amines. The origin of 1294.90 cm\(^{-1}\) as yet completely understood. It has never been thought but it perhaps linked with various stretching and bending vibrations associated with C-N single bond. The vibration band at 1112.25 cm\(^{-1}\) is arises due to presence of C-N double bond and indicative of protonation. This peak is much pronounced significantly in case of FTIR spectra of polyaniline. The vibration band at 793.45 cm\(^{-1}\) is attributed to C-H vibration band of paralinked phenyl ring. It confirms the predominance of para coupling in polymerization of aniline.

3.4 Synthesis of MWCNT doped PANI Nanocomposites

MWCNT doped PANI nanocomposites are also synthesized by following same chemical reaction and condition with concentration of 1% wt and 3% wt MWCNT. These synthesized MWCNT doped PANI nanocomposites are characterized with FTIR spectroscopy for identification chemical composition. The observed FTIR spectra of synthesized MWCNT doped PANI nanocomposites are discuss in following.

3.4.1 FTIR Spectroscopy of MWCNT doped PANI Nanocomposites

The FTIR spectra of MWCNT doped PANI nanocomposites are shown in Figure 3.6. The peak at 835 cm\(^{-1}\) is attributed to the N–H out-of-plane bending absorption. Presence of benzoid band around 1470 cm\(^{-1}\) and quinoid vibration around 1580 cm\(^{-1}\) indicate the emeraldine salt form of PANI and MWCNT doped PANI nanocomposites. The band at ~3400 cm\(^{-1}\) indicates stretching of N-H band of aromatic ring in PANI and its composites. A striking difference between spectra of PANI and MWCNT doped PANI nanocomposites is found. The signal near this region ~3400 cm\(^{-1}\) is broad as well as strong in the composite samples (significant in 3wt% MWCNT doped PANI) yet very weak in pure PANI spectra.

The peak at around 1590 cm\(^{-1}\) is corresponds to the IR active phonon mode of the MWCNT and the peak at around 1730 cm\(^{-1}\) corresponds to the stretching mode of the
carboxylic acid groups which indicate the formation of carboxylic acid groups at both ends and on the MWCNTs, responsible for mixing MWCNT with PANI [41-42]. The strong band at near 1150 cm\(^{-1}\) as the electronic like band and is considered to be a measure of the degree of delocalization of electrons [43] and thus it is characteristics peak of PANI conductivity. All peaks obtained are same as studied in literature [44].

The intensity of peaks in composites spectrum is increased, and shifted relative to peaks observed in case of pure PANI. These indicates the increase of the designated, electronic like absorption peaks defined as (\(-\text{N=quinoid}=\text{N-}\)) are in good agreement with our increased conductivity measurements behaviour.

![Figure 3.6: FTIR spectrum for (a) Pure PANI (b) 1% wt MWCNT doped PANI and (c) 3% wt MWCNT doped PANI nanocomposites](image)

It shows that the interaction between PANI and MWCNT doped PANI increases with effective degree of electron delocalization which results in enhance the conductivity, strong interaction may also result in carbon nanotubes functioning, as a chemical dopant for PANI conductivity. Also pure PANI, MWCNT doped PANI nanocomposites shows reduced ratio of benzoid to quinoid intensity indicating the stabilized form of MWCNT doped PANI nanocomposites and hence possible increase of conductivity.
As we all know, any material in its nano form is more demandable than in its bulk form because in nano level the material undergoes a drastic change in its property and has versatile application. Thus zinc oxide (ZnO) which is a multifunctional material with a large direct band gap created anxiousness in the scientific minds to enhance the research on one dimensional nanostructure especially oxide materials. The properties of zinc oxide makes the material eligible exists in various shapes in the form of nanostructures exhibiting a varieties of properties like piezoelectricity, optical transparency, conductivity, solar cell, UV and visible photoluminescence, optical nonlinearity and many more. But obtaining various shapes of nanostructures merely depends on different processing techniques. Methods which are related to the synthesis of various shapes of zinc oxide nanostructures are chemical and thermal vapour deposition laser ablation, vacuum arc deposition, electrochemical, and hydrothermal process. But all these methods reported possesses many complex steps; require sophisticated equipments and rigorous experimental conditions [44]. Thus need for a synthesis technique arises which would be simple and by using it zinc oxide nanostructures can be grown in a laboratory environment and also characterized such structures for a wide range of applications through repeated fabrication and modification. One such inexpensive method which can be implemented without having any complexes and need for sophisticated equipments is also not desirable is the wet chemical method. Not only the method enable us to fabricate multi-dimensional nanostructures in a large scale but also provides repeated preparation that enables one to varying the process conditions for an investigational study and repeatability in the yield. Till now there were number of reports regarding the fabrication of one dimensional ZnO nanostructures especially nanorods and nanotubes via number of routes. Some of them are Mohanta et al. have reported the fabrication of ZnO nanorods grown on P-type GaN/sapphire and silicon-on-insulator substrates by chemical vapour deposition [45]. The nanorods show strong UV band edge emission around 380 nm [46-48]. In another report by Ding et al., ZnO nanorods have been grown on various substrates (ceramic, glass, Si, metal) by solution phase growth at 95°C [46]. However there are only few reports on the fabrication of ZnO nanobelts by VLS and thermal evaporation method [49-51]. Zhang et al. have fabricated
ZnO nanobelts by thermal evaporation of ZnCl₂ at 700°C under flow of Ar and O₂ [51]. VLS method is also adapted to fabricated ZnO nanobelts, but only very few literature are there which talks about the fabrication of ZnO nanobelts by chemical/ hydrothermal method.

But as this chemical method is concerned it is found to be very simple, cost-effective and quite suitable to adopt in the laboratory without much infrastructures. By adapting this method it has been possible to grow ZnO nanobelts at room temperature over a very short duration of growth of 4 hrs only and without using any surfactant or catalyst not only this much but this method does not necessitate the maintenance of rigorous experimental conditions as in the earlier cases [52-53]. Therefore, overall we can conclude that synthesis of ZnO nanostructures by chemical route not only provides a method for large-scale fabrication of ZnO nanorods with a low cost, but also open a way to the size-controlled fabrication of other materials.

Roy et al.. [54] preparation of zinc oxide nanoparticles loaded in various weight percentages in ortho-chloropolyaniline by in situ polymerization method. The length of the O- chloropolyaniline tube is found to be 200 nm and diameter is about 150 nm where in the embedded ZnO nanoparticles is of 13 nm as confirmed from scanning electron microscopy as well as transmission electron microscopy characterizations. The presence of the vibration band of the metal oxide and other characteristic bands confirms that the polymer nanocomposites are characterized by their Fourier transmission infrared. The X-ray diffraction pattern of nanocomposites reveals their polycrystalline nature. Electrical property of nanocomposites is a function of the filler as well as the matrix. Cole–Cole plots reveal the presence of well-defined semicircular arcs at high frequencies which are attributed to the bulk resistance of the material. Among all nanocomposites, 30 wt% shows the low relaxation time of 151s, and hence it has high conductivity.

Kumar et al. [55] reports a facile and large-scale synthesis of ZnO nanoparticles by simple self-propagating solution combustion method using dextrose. The prepared ZnO nanoparticles were characterized by various analytical tools using field emission scanning electron microscopy (FESEM) attached with energy dispersive spectroscopy (EDS), X-ray diffraction (XRD) pattern, Fourier transform infrared (FTIR) spectroscopy and UV-Vis.
spectroscopy measurements. The detailed characterizations confirmed that the prepared ZnO nanoparticles are pure, well-crystalline and possessing wurtzite hexagonal phase.

Kondawar et al. [56] used a simple approach for the formation of Zinc oxide (ZnO) nanoparticles is described. The particles of the synthesized zinc oxide are in spherical nano-sized form as confirmed from its TEM characterization. Composites of different molar concentration of aniline and ZnO nanoparticles have been prepared. During the polymerization of the monomer (aniline) by using oxidizing agent (ammonium persulphate) and dopant ($\text{H}_2\text{SO}_4$) under constant stirring at 0-4°C, synthesized nanostructure zinc oxide powder was added. The presence of the vibration band of the dopant ion and other characteristic bands confirm that the polymer nanocomposites are in conducting emeraldine salt phase as characterized by their FTIR. Nanocomposites reveal polycrystalline nature and show homogeneous distribution of zinc oxide in PANI. The electrical property of nanocomposites is a function of the filler as well as the matrix. In the case of ZnO doped PANI nanocomposites, ZnO is semi-conducting; the electrical conductivity is predominantly due to the PANI. Composites exhibit resistivity in between pure PANI and the ZnO nanoparticles. The change in the resistivity of the composites indicates a change in the doping state of the polymer. The composite PANI-ZnO (1:1) shows higher conductivity as compared to other ratios.

Ansari et al. [57] report that nanocomposites of polyaniline and zinc oxide nanoparticles using polycarbonate as supporting matrix were prepared by direct mixing process. These nanocomposites were studied for their DC electrical conductivity using four-in-line probe technique. Stability of DC electrical conductivity in terms of electrical conductivity retention was also studied using two slightly different techniques. The nanocomposites were also characterized using FTIR, SEM, TEM, and XRD. It was found that the electrical conductivity of the nanocomposites first increased with the increase in concentration of ZnO nanoparticles content, but then decreased on further increase in its content. Stability studies showed that the loss in electrical conductivity decreased with increase of ZnO content in nanocomposites. TEM and XRD results showed that nanoparticles are uniformly distributed in polymer matrix and also suggest that the direct solution mixing method may be adopted as an easy and efficient route for the preparation of nanocomposites.
3.5.1 Synthesis of ZnO

In order to synthesize ZnO nano-particle, Zinc nitrate hexahydrate, dextrose is purchased from Sigma Aldrich and deionized Water. The synthesis of zinc oxide nanoparticles was done by facile self-propagating solution combustion method. In a typical synthesis process, 0.05 M zinc nitrate hexahydrate (Zn(NO$_3$)$_2$· 6H$_2$O) (10 ml) was mixed well with 0.05 M aqueous solution of dextrose (10 ml) at room temperature. After 30 min of vigorous stirring, the solution was filtered and then transferred to a china dish which was then placed in a preheated muffle furnace at 400°C. The contents ignite and form highly spongy material which was further annealed in muffle furnace at 700°C for 30 minutes.

3.5.2 FTIR Spectra for Pure ZnO

The chemical composition of ZnO nanoparticle analyzed by Fourier transform infrared (FTIR) spectroscopy is shown in Figure 3.7.

![Figure 3.7: FTIR spectrum synthesized ZnO nanostructures](image)

Well defined bands at 538, 833, 1630 and 3467 cm$^{-1}$ appeared in the FTIR spectrum. The origination of a well-defined band at 538 cm$^{-1}$ is due to metal-oxygen (Zn-O) modes and hence confirms the formation of ZnO. The appearance of a short band at 833 cm$^{-1}$ in the spectrum are due to in-plane bending vibration of NO$_3^-$ ions [58-59], presence
of two more bands in the spectrum at 1630 and 3467 cm\(^{-1}\) are due to the bending vibration of absorbed water and surface hydroxyl, and O-H stretching mode respectively.

### 3.5.3 Synthesis of ZnO doped Polyaniline Nanocomposites

Synthesized polyaniline and 1%, 3% weight percentage ZnO (according to monomer ratio) were taken in two voils and sonicated for 1 hour to mix together. Now sonicated composites were washed several times with methanol and dried in oven. The obtained composites were further characterized for structural, compositional optical and dielectric properties as below.

### 3.5.4 FTIR Spectra for ZnO doped Polyaniline Nanocomposites

The FTIR spectra of pure PANI and ZnO doped PANI nanocomposites are shown in Figure 3.8. The peak at 835 cm\(^{-1}\) is attributed to the N–H out-of-plane bending absorption. Presence of benzoid band around 1470 cm\(^{-1}\) and quinoid vibration around 1580 cm\(^{-1}\) indicate the emeraldine salt form of PANI and ZnO doped PANI nanocomposite.

The band at 3400 cm\(^{-1}\) indicates the stretching of N-H band of aromatic ring in PANI and its composites. The peaks obtained for ZnO doped PANI nanocomposites are shift to higher wave number which indicates the interaction between pure PANI and ZnO [60-62]. As compared to pure PANI, ZnO doped PANI nanocomposites shows reduced ratio of benzoid to quinoid intensity indicating the stabilized form of ZnO doped PANI nanocomposites.

From above detail discussion of review literature about pure and doped EAP, we synthesized pure as well as CNT and ZnO doped EAP successfully and confirm chemical composition by using FTIR spectra. The peaks obtained for pure and doped synthesized EAP are similar as studied in literature. Now, these synthesized pure and doped EAP composite are used for different physical properties measurement in preceding chapters.
Figure 3.8: FTIR spectrum spectra for (a) pure PANI, (b) 1%wt ZnO doped PANI and (c) 3% wt ZnO doped PANI nanocomposites.

3.6 Conclusion

This chapter represents the detail inspection of literature survey of EAP and its composites based on the research work carried out by various research groups in the area describing their synthesis procedure, physical properties and effect of dopant on properties of these materials. Further, synthesized pure and doped EAP are characterized by using FTIR spectroscopy which reveals and confirm the synthesis of EAP.
Bibliography