CHAPTER 7

SUMMARY AND CONCLUSION

In the modern era of scientific world highly sophisticated instrumental techniques of spectroscopy such as Infrared, Raman, NMR, UV-Vis and Photon correlation spectroscopies have profound applications in many branches of science. The vibrational spectroscopy is well established as powerful technique in the precise identification and structural confirmation of organic, inorganic, and crystalline polymeric and coordination compounds. The development of the Raman and infrared has led to the renaissance in the vibrational spectroscopy. NMR spectroscopy is arguably the most important technique available today for chemists and physicists for analysis of liquids and solids (including polymers). These are one among many valuable physical methods currently available to the researchers and experimenters in the field of spectroscopy which is based on the interaction of electromagnetic radiation.

The present thesis is devoted entirely to the proper use of infrared, Raman, $^{13}$C NMR, UV-Vis and Photon correlation spectroscopies for the characterisation of silver nano particles. The above said techniques are used for the analysis of polymer structures after it is blended with nanoparticles. Further a systematic approach has been adopted for the study of antibacterial activity of wound dressing material prepared using the polymer nanosilver composite.

The chapter one presents an introduction to nanotechnology and its applications. Nanoparticles are a unique subset of the broad field of nanotechnology that includes any type of particles with at least one dimension
less than 100nm. Nanoparticles play an important role in a wide variety of fields including advanced medicine, pharmaceuticals and environmental detection and monitoring.

The second chapter provides an insight to various principles involved to allow an understanding of FTIR, Laser Raman, UV-visible, $^{13}$C NMR and photon correlation spectrometry. The main emphasis has been put on the theory and practice of these instrumentation methods.

In the third chapter synthesis of silver nanoparticles was done and characterisation of the particles was carried out using scanning electron microscopy (SEM), Photon correlation spectroscopy, Fourier transform infrared spectroscopy and UV-Vis spectroscopy. The size of the particle is determined by scanning electron microscopy and Photon correlation spectroscopy. The Zeta potential and the size of the nano particles are determined by Zeta size analyser in the range of 0.3 to 10 microns. The Zeta potential for the silver suspension was found to be +40.8. This confirms that silver particles are more stable in the suspension. The SEM image with a magnification range of 15 to 2,00,000 times and with resolution of 2nm, confirms the average size of the particles to be in the range of 95nm.

FTIR spectrum in the range 400 cm$^{-1}$ to 4000 cm$^{-1}$ was recorded and the vibrational band assignments are carried out. Vibrational frequencies are found to be in good agreement with the previous works. The diffused UV absorption spectrum of silver nano particles was recorded over the region
100 nm – 1000 nm. A characteristic strong absorption band with a maximum at 420 nm was observed. Thus characterisation of nano particles was done by different methods.

The **fourth chapter** is entirely devoted for the selection of a proper binding material for making a wound dressing mat with nanosilver particles. Polyvinyl pyrrolidine (PVP) is a water soluble polymer with a large number of consumer uses. The main objective of this chapter is to evaluate the microstructure of PVP nano silver composite employing FTIR, laser Raman, UV-Vis, $^{13}$C NMR spectroscopy and scanning electron microscopy in order to understand the blend behavior of polymer with silver nano particles.

The FTIR spectrum is recorded in the range 400 to 4000 cm$^{-1}$. The FTIR spectrum for pure PVP clearly indicates that the observed absorption peaks corresponds to the chemical bonds present in PVP. The peak at 1210 cm$^{-1}$ represents C-N functional unit present in PVP. Extra bands occur at 1200 cm$^{-1}$ and 1220 cm$^{-1}$ after embedding of silver nanoparticles with PVP. The extra peaks corresponding to C-N bonds may be attributed due to chemical coordination of silver nanoparticles. Another two peaks at 1629 cm$^{-1}$ and 1637 cm$^{-1}$ in pure PVP due to C=O bonds becomes narrower and shifts to 1645 cm$^{-1}$ after bonding with Ag nanoparticles. The peaks in the Raman spectrum also support the vibrational band assignments. The change in wavenumber of C=O bond may occur due to the bond weakening. As a result of back bonding via partial donation of lone pair electrons from oxygen in PVP to vacant orbital of Ag. No appreciable
change has been observed for other peaks. This confirms the coordination and conjugation of embedded Ag nanoparticles with N and O atoms of C-N and C=O bonds respectively, which results in the observed changes in optical behavior of host PVP.

Pure PVP is a transparent compound which does not alter in colour with time. It is stable in 400-800 nm wave length. Thus no absorbance maxima for pure PVP is found in the region 400-700nm. Due to this characteristic PVP forms a blend with AgNO₃. The UV spectra of the composition exhibits the characteristic maxima which is only due to silver nano particles. The presence of PVP does not affect the absorbance maxima. Further the Stability of PVP and AgNO₃ composite was analysed periodically every month, until six months. The stability of the solution remains unaltered even after six months. This is verified by UV absorption spectra recorded at the end of every month. ¹³C NMR data agrees well with the FTIR results and there is new bond formation in the complex. These results show that PVP can act as a good binder for Ag nano particles. The above results were cross checked by using ¹³C NMR. The signals from 60-62 ppm in NMR are assigned to carbon shift. With reference to the previous works on shifts of carbon atoms in related compounds the shift of C-C is assigned to doublet 46.590 ppm and 46.698 ppm. The C-N signal is present at 45.902 and 45.550 ppm. The values of the chemical shift for the composite did not change
compared to that of pure PVP. Finally the SEM image also confirms that PVP is a good binding agent for silver nanoparticles.

The **fifth chapter** is largely concerned with the characterisation of the sodium polyacrylate polymer and sodium polyacrylate with nano silver composite. Acrylates and acrylic chemistry have a wide variety of commercial and industrial uses. Sodium polyacrylate are referred to as “super absorbants”. The approach adopted for the characterisation is, the analysis of infrared, UV visible, $^{13}$C NMR, Laser Raman spectra and SEM image. To proceed in the right way first a vibrational analysis of pure sodium poly acrylate polymer and nano silver sodium poly acrylate composite was carried out by FTIR and Laser Raman spectroscopy in the range of 400-4000 cm$^{-1}$.

A wide band corresponding to stretching vibrations of the hydroxyl group (band of a free OH group[from water] and hydrogen bonds) occurs in the range of wave number 3700-3100 cm$^{-1}$ in pure sodium polyacrylate. An exchange of ions is accompanied by conformation changes in the polymer structure. In the range of wave numbers 3155-3561 cm$^{-1}$ a certain decrease of the absorption band corresponding to stretching vibrations of -OH groups can be observed in the sodium polyacrylate and Ag nano particle composite. It is caused by water evaporation from sodium polyacrylate solution. Three bands at 1575 cm$^{-1}$, 1616 cm$^{-1}$ and 1629 cm$^{-1}$in the spectra of pure sodium polyacrylate typical for salts of carboxylic acids (symmetrical stretching vibrations of carboxyl anions – COO ) occur at 1566,1635 and 1643
cm\(^{-1}\) in the composite on the obtained FT-IR spectra. Small changes in the shape of those bands in the composite indicate structural conformation changes, occurring during material hardening due to building-in of Ag\(^+\) cations in place of Na\(^+\) cations in a polymer chain. Intensities and position changes of the band, after hardening, can be attributed to water evaporation and to vibrations of hydrogen bonds of O-H type. Sodium polyacrylate undergoes change after it is blended with silver nanoparticles. These changes are observed from the laser Raman and infrared spectrum.

The UV absorbance spectrum was recorded in the region 200-700 nm using UV 3600 spectrophotometer. In UV absorption spectrum of sodium polyacrylate exhibits its own characteristic peak lowering the absorption intensity of silver nanoparticles in the composite. Further a six month UV analysis of the composite shows a decrease in the absorbance of sodium polyacrylate.

Sodium polyacrylate structure before and after making composite with Ag nano particles was confirmed by \(^{13}\)C NMR signals. The peaks of 177.835, 177.654, 177.409, and 177.167 ppm originated from carbon atoms of carbonyl group in carboxylic acids. These signals remain unchanged in the composite also. Three signals 45.844ppm, 44.725ppm and 44.410 ppm can be assigned to \(C_\alpha\) carbon atoms while signals 35.319 ppm, 34.782 ppm and 33.773 ppm belong to \(C_\beta\). But in the nano composite spectrum there is one more signal observed at 42.619 ppm along with the characteristic signal.
These new signal appearing in the NMR may be due to Ag ions building into a polymer chain with carbon atom. The above results show that a formulation made of sodium poly acrylate and nanosilver can impart properties such as absorption of moisture and antibacterial property. A formulation using sodium polyacrylate and nano composite can be used for diabetic patients where a fast recovery of wound is required.

The aim of chapter six is to prepare a formulation containing nano silver particles and PVP, which could be applied for wound dressing materials. Silver ion has been used for centuries to prevent and treat a variety of diseases and infections. In recent years, extensive studies have been undertaken on the use of antibacterial properties of silver incorporated within medical gadgets. PVP and silver nanoparticles composite were prepared by standard methods. A wound dressing material is prepared by Electrospinning process using Silver nanoparticles and PVP composite solution. The prepared fiber consists of 0.24 mg of silver per mg of PVP. The fiber is a binary alloy of silver and oxygen with negligible contaminants. This unique structure in combination with oxygen atoms /molecules that are trapped in the lattice contribute to the enhanced solubility of the films which continue to release silver until the concentration in solution reached 66mg/L a level that is 50 to 100 times higher than is expected from typical bulk pieces of silver metal.

In vitro antibacterial tests were performed using Escherichia coli (E. coli) and Staphylococcus aureus (Stap) to determine the antibacterial
capability of the Ag/PVP fibrous membranes. The strains were prepared for testing antibacterial activity of membrane. All specimens were prepared with the diameter of 5mm for antibacterial test. The anti bacterial activity of untreated wound dressing and silver treated wound dressing were observed and compared periodically for every 2 hrs. Inhibition clear zones started increasing in diameter and after 2 hrs the width of E.coli and stap increased to 1.2 mm and 1.5 mm respectively. The antibacterial activities of the Ag/PVP membranes on the E.coli and Stap were compared with the silver untreated wound dressing memberanes. The result proves that, silver treated fibrous membranes shows strong antibacterial properties.

On the basis of the observations and findings above, it can be concluded that PVP is a good matrix for containing and gradually releasing silver nano particles. Silver ions interact with the thiol groups of enzyme and proteins that are important for the bacterial respiration and the transport of important substance across the cell memberanes and within the cell and kills the bacteria. In conclusion, the present research work is a systematic approach to synthesis and characterisation of silver nanoparticles. It also presents significant application of spectroscopy in the selection of binders for the wound dressing materials made of silver nanoparticles. In future this research work can be extended to prepare a wound dressing material with sodium poly acrylate using Electrospinning process and test its antibacterial property and antiviral properties.