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¹³C NMR and FTIR spectroscopic study of blend behavior of PVP and nano silver particles

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ABSTRACT

Nanotechnology is the most promising field for generating new applications in medical field. Silver ion has been used for centuries to prevent and treat variety of diseases and infections. In this study we have selected Polyvinyl pyrrolidone (PVP) as a binder for nano silver particles. This was done with the aim to investigate the blend behavior of PVP with nanoparticles which can have their application in medical field. PVP is a water soluble polymer with a large number of consumer uses. This commercial success derives from its biological compatibility, low toxicity, film-forming and adhesive characteristics, unusual complexing ability, relatively inert behavior toward salts and acids, and its resistance to thermal degradation in solution. Because of these diverse properties, FTIR and ¹³C NMR are employed successfully to study the blend behavior of PVP with nanosilver. FTIR spectrum is recorded in the range 400-4000cm⁻¹. The characteristic vinyl bands are observed in the region 965 cm⁻¹ and C-C, C=O stretching and bending are found in the appropriate region in pure PVP and PVP and Nano silver complex. The ¹³C NMR provides valuable information about the structure of the complex. FTIR and NMR studies confirm that structure of the complex is stable and the characteristic bands of PVP are not disturbed by the presence of silver ions. Thus this study suggest that a product made of PVP and nanosilver composite can be used as external formulation such as wound healing in medical field.

Key words: silver nano particles, FTIR, NMR, blend behavior.

INTRODUCTION

Polyvinyl pyrrolidone (PVP) which is among the most known biocompatible polymers, has long been intense use in medicine, as a blood preservative, a detoxification material, a binding agent

for a large number of pharmacological preparations, thickeners for liquid drugs, and a shell for the targeted delivery of drugs and preparation of bioactive ointments and creams in cosmetics [1-4]. Application in medicine improves high requirements on the purity of polymer and its mechanical properties. PVP was initially used as a blood plasma substitute and later in a wide variety of applications in medicine, pharmacy, cosmetics and industrial production [5,6]. PVP is a biopolymer with molecular formula $(C_6H_9NO)_n$. It is white to light yellow, hygroscopic, amorphous powder. It has a density of 1.2g/cm^3 . It is soluble in water and other polar solvents. When dry it is a light flaky powder, which readily absorbs up to 40% of its weight in atmospheric water. In solution, it has excellent wetting properties and readily forms films. This makes it good as a coating or an additive to coatings. PVP is stabilizer and has E number E1201. One of the special properties of PVP is its universal solubility both in hydrophobic and in extremely hydrophilic solvents. PVP products are soluble in water and polar solvents. Due to its outstanding properties we selected PVP as a binder for nano particles [7-9] which can be used for medical applications.

MATERIALS AND METHODS

PVP was purchased from Sigma Aldrich laboratories. Synthesis of nano particles was done using standard methods. Nano silver particles of range 100-200nm were used for making PVP nano silver composites. For optical characterization of pure PVP, and PVP nano composite composites FTIR 8600 model spectrometer in the range of $400\text{-}4000\text{ cm}^{-1}$ was used.

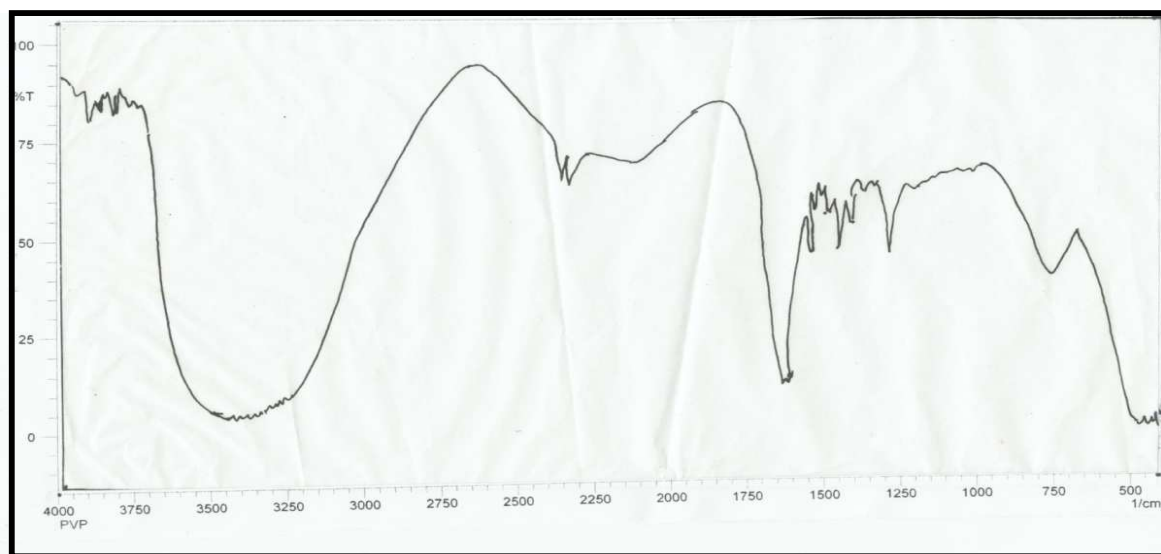


Fig 1 The FTIR spectrum of pure PVP

The assignments are discussed below for pure PVP and PVP nanosilver composite separately in order to confirm the blend behavior. Pure PVP spectrum is exhibited in the fig 1. The FTIR spectrum of PVP nanosilver composite is exhibited in fig 2. ^{13}C NMR of PVP and PVP nanosilver composite are recorded at IISc, Bangalore using Bruker DRX-500MHz spectrometer. Polymer samples were dissolved in D_2O and recorded with a delay of 2.5sec. The spectral recordings of different regions are given in figures 3. and 4. The signals corresponding to various groups are tabulated in the table 1.

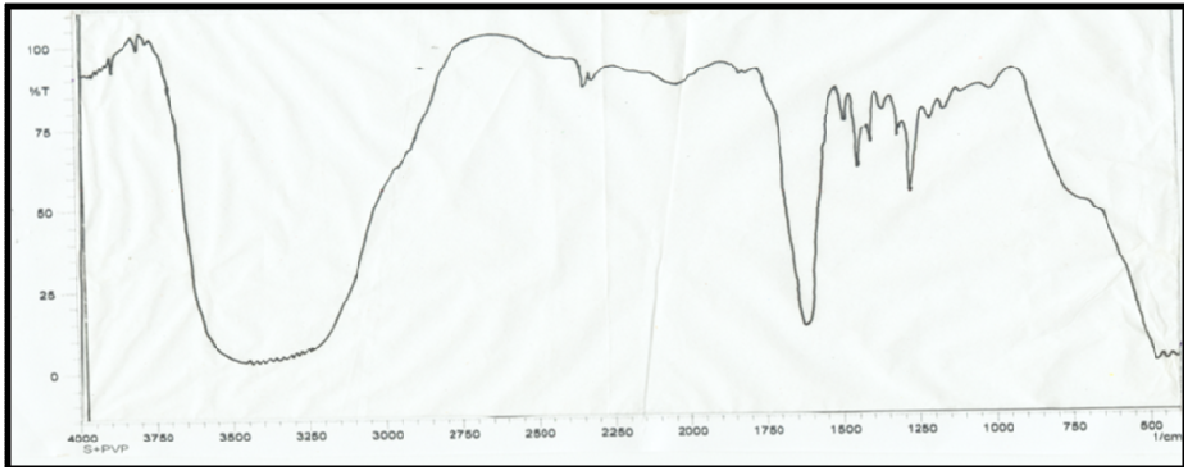


Fig 2 The FTIR spectrum of PVP/Silver nano particle composite

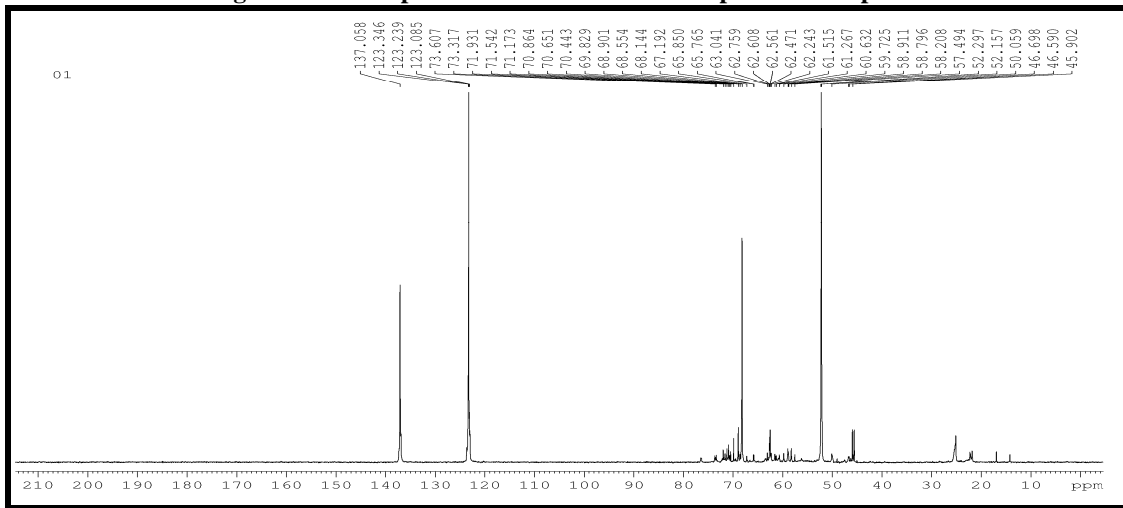


Fig 3 The NMR spectrum of pure PVP

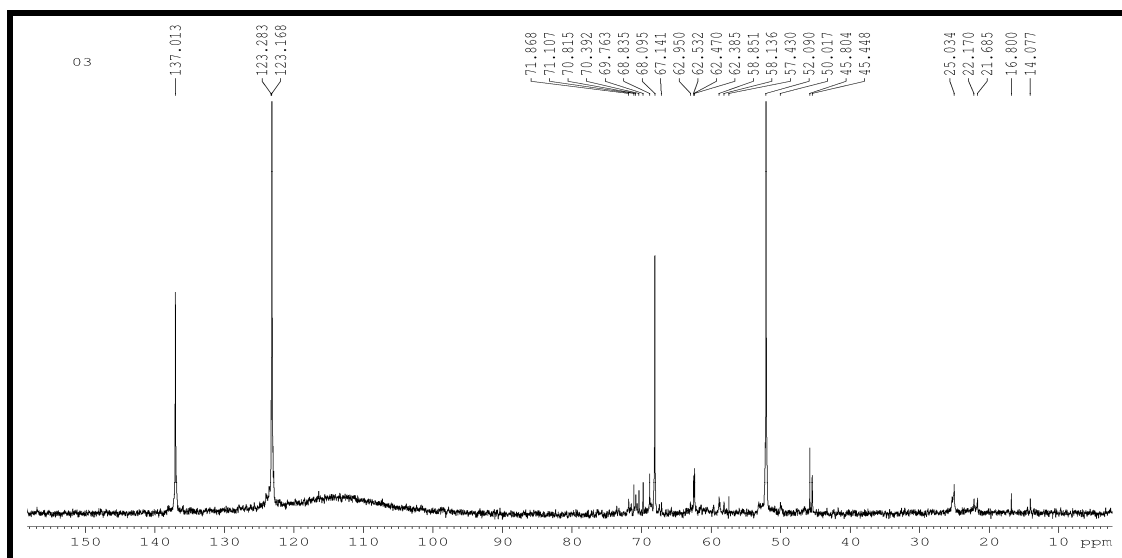


Fig 4 The NMR spectrum of PVP/Silver nano particle composite

RESULTS AND DISCUSSION

Fourier Transform Infrared spectroscopy and NMR spectroscopy is a very useful technique to examine the structure and structural transformation of materials Using the above two techniques a detailed vibrational analysis is carried out for pure PVP and PVP nanosilver composite.

a) C-C Vibrations

In the most of the mononuclear and polynuclear aromatic compounds the ring carbon-carbon stretching vibrations occur in the region 1625-1530 cm^{-1} [10-13]. In the spectrum of PVP, the bands appearing in the region 1500-1600 cm^{-1} are assigned to this mode. In the PVP nanosilver matrix the bands 1500 and 1520 cm^{-1} are identified in the same region. The bands

Table 1 Comparison of FTIR and NMR vibrational assignments. PVP and Nano silver Composite

S. No	FTIR Frequencies (cm^{-1})	NMR Chemical Shift (ppm)	Assignments
1	430 - 760	46.59 – 46.09	C - C
2	1210	45.09 – 45.550	C - N
3	1629	137.08	C = C Ring
4	1425 – 1475	73.31 – 73.60	CH_2
5	3278	65.850 – 63	CH_3
6	3278	21- 25	CH_3

in the aromatic ring deformation region are quite sensitive to change in the nature and position of the substituents although other bands depend mainly on the distribution and number of substituents rather on their chemical nature or mass. So that these latter vibrations together with, out of plane vibrations of the ring of hydrogen atoms are extremely useful in determining the position of substituents [14]. The C-C out of plane ring deformation vibration occurs in the region 397-515 cm^{-1} in the aromatic compounds. With reference to the previous works the bands observed in the region 437- 499 cm^{-1} has been assigned to C-C out of plane deformation and the infrared peak at 760 cm^{-1} is assigned to C-C in plane bending in pure PVP. In the PVP nanosilver matrix C-C out of plane deformation is found in the region 430- 486 cm^{-1} whereas C-C out plane bending occurs in the region 725 cm^{-1} which is deviated due to the presence of PVP nanosilver matrix bonding.

b) C-H Vibrations

The ring C-H vibrations for benzene derivatives occur in the region 3080-3010 cm^{-1} . The bands have strong and medium intensity [15]. In the present molecule the observed bands in the region 3294 cm^{-1} are assigned to this mode. PVP nano silver matrix spectrum shows the C-H vibrations almost in the same frequency range.

A number of C-H in plane deformation bands occur in the region 1290-1000 cm^{-1} the bands are usually being sharp but weak to medium intensity [16]. However these bands are not important for interpretation purpose although they can be used quantitatively. In fact a number of interactions are possible, thus necessitating a great care in the interpretation of bands in the region. The frequencies of C-H out of plane deformation are mainly determined by the number of adjacent hydrogen atoms in the ring and not affected by the nature of the substituent group. In the present molecule these vibrations are found in the region of 1290 and 1210 cm^{-1} . In the PVP –nano silver matrix the bands in the region 1210 - 1240 cm^{-1} and 1260 cm^{-1} are assigned to this mode.

c) C-N vibrations

Silverstein et al [17] assigned C-N stretching absorption in the region 1342-1266 cm^{-1} the spectra of benzene and substituted compounds exhibit the band in the region 1220 cm^{-1} . Further some of the phenol derivatives exhibit the same band in the region 1117 and 1152 cm^{-1} . In analogy with the previous workers the band in the region 1190 and 1210 cm^{-1} are assigned to C-N stretching. But in PVP nano silver composite two bands of almost same intensity occurs in 1200 and 1220 cm^{-1} . Based on the results of the previous work on benzene derivatives the bands of the IR spectra 462- 491 cm^{-1} are assigned to C-N bending vibration modes. The bands in the region of 470 and 486 cm^{-1} in PVP and PVP nano silver composite has been assigned to symmetric C-N bending.

d) C=O vibrations

The C=O vibrations of dienes are reported by earlier workers in the region 1600-1625 cm^{-1} [18]. In the present molecule the strong bands in the regions 1629 and 1637 cm^{-1} are assigned to this mode. Instead of two peaks in PVP only one peak in 1645 cm^{-1} appears in PVP nano silver matrix.

e) Vibrations of the hydroxyl group

Hydroxyl groups which are hydrogen bonded to aromatic ring absorb at 3580-3480 cm^{-1} . With stronger intermolecular bonding the O-H stretching vibrations may give rise to broad and intense bands which are often overlaid with peaks due to Fermi resonance interactions. The O-H stretching frequency decreases as the hydrogen bond association becomes stronger and vice versa. In the present molecule the O-H stretching falls in the region 3180-3527 cm^{-1} . The O-H Vibrations almost occur in the same region in PVP nanosilver composite.

f) Study and analysis of FTIR and NMR spectrums.

Carbon atoms form the skeleton of an organic molecule; hence information about them is very useful for the identification of the structure of an unknown compound. ^{13}C NMR spectrum provides valuable structural information. According to the spectra, the carbonyl region presents different split -ting as a response of microstructure assignment Spectrum shows signals that are broader than those in water, which is attributed to the strength of polymer/solvent interaction. NMR analyses as carbon atoms form the skeleton of an organic molecule any structural variation of an organic molecule will be evident in its ^{13}C spectrum. The range of chemical shifts of a substituted benzene ring is about 60ppm in ^{13}C spectrum. It may slightly increase or decrease depending on the substituent groups [19]. The signals from 60-62 ppm are assigned to carbon shift in the present work. With reference to the previous researchers on some shifts of carbon

atoms in pyridine related compounds the shift of C-C is assigned to doublet 46.698 ppm and 46.590 ppm. The C-N signal is present at 45.902 and 45.550ppm [20].

A sharp signal due to C-H shift is observed 68.144ppm. Due to carbon atoms in the ring signals from 123.085ppm 137.058 ppm are observed. There is a doublet which corresponds to 73.317 and 73.607ppm which indicates the presence of hydrogen connected to the carbon in CH₂. A doublet present at 65.850 and 65.765 and signals from 21-25 ppm corresponds to CH₃ – group [21-23]. It is worth pointing out that all signals are narrow, which can be evidence that some miscibility between components of blends can be occurring. The carbonyl bends signals also showed distribution sequences of microstructures that can be assigned in the systems. Both the number and values of chemical shift for these microstructures did not change comparing to those of the initial polymers because the interaction process occurs with the same strength for all types of carbon, as it is an unselective process. Appearance of additional shifts in PVP/Ag nano composite may due to the formation of new bonds with carbon atoms.

CONCLUSION

The FTIR spectrum for pure PVP clearly indicates that the observed absorption peaks correspond to the characteristic chemical bonds present in PVP. The peak at 1190 cm⁻¹ represents the functional unit C-N present in PVP, shifts to 1210 cm⁻¹ after embedding of silver nanoparticles. The peak shifting corresponding to C-N bond towards higher wavenumber may be attributed due to chemical coordination of Ag nanoparticles with C-N bond.

Another two peaks at 1629 and 1637 cm⁻¹ in pure PVP due to C=O bonds becomes narrower and shifts to 1645 cm⁻¹, after the formation of Ag nanoparticles within PVP matrix. Such a 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. Further no appreciable change has been observed for other peaks marked. This confirms the coordination and conjugation of embedded Ag nanoparticles with N and O atoms of C-N and C=O bonds, respectively of this polymer, which results in the observed changes in optical behavior of host PVP matrix. 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.

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REFERENCES

- [1] Cao, G. (2004). Nanostructures and Nanomaterials. *Imperial College Press*.
- [2] Chou, K.-S., Lu, Y.-C., and Lee, H.-H. (2005). Effect of alkaline ion on the mechanism and kinetics of chemical reduction of silver. *Science Direct*.
- [3] Frattini, A., Pellegrini, N., Nicastro, D., and de Sanctis, O. (2005). *Preparation of polychrome silver nano particles in different solvents*. Journal of Materials
- [4] Grijalva, A. S., Urbina, R. H., Silva, J. F. R., and Borja, M. A. (2005). Ethylene glycol

silver nitrate polyvinylpyrrolidone. *Science Direct*.

- [5] Jain, P. and Pradeep, T. (2004). Potential of silver nanoparticle- coated polyurethane foam as an antibacterial water filter. *Wiley InterScience*.
- [6] Jiang, Z.-J., Liu, C.-Y., and Sun, L.-W. (2004). Catalytic properties of silver nanoparticles supported on silica spheres. *American Chemical Society*.
- [7] Klein, M. V. and Furtak, T. E. (1986). *Optics*. Wiley.
- [8] McFarland, A. D. and Duynes, R. P. V. (2003). Single silver nanoparticles as real-time optical sensors with zeptomole sensitivity. *Nano letters*.
- [9] A. Anjaneyulu and G. Ramana Rao, *Spectrochim Acta* (1998).
- [10] Tufts, L.E., Davis, A. in "Progress in infrared spectroscopy" Vol. I, H.A. Szymanski (ed.), Plenum, Press (1998) New York 151,
- [11] Varsanyi, "Assignments for vibrational spectra of seven hundred benzene derivatives", Vol I (Adam Hilger, London) (1974) pp 109-442 and the references cited therein.
- [12] G. Socrates, *Infrared characteristic frequencies*, John Wiley and Sons. New York.
- [13] R.R. Randle, D.H. Whiffner, *J. Chem. Soc.*, London, (1952), 1453.
- [14] M. Silverstein, G., Clayton Bassler and C. Morill, *Spectrometric identification of organic compounds* John Wiley, New York, (1981).
- [15] G. Venkata Ramana Rao and G. Ramana Rao, Vibrational spectra and Normal co-ordinate treatment of 2,5-Dihydroxy Toluene and 2,6-Dihydroxy Toluene, *Proceedings of NCONS 97*, (1997), 193.
- [16] J.W. Brooks and J.F. Morman *J. Chem. Soc.*, (1961), 3372.
- [17] W.F. Baitinger et al., *Tetrahedron*, 20, (1964), 1635.
- [18] Text book of *NMR—From Spectra to Structures an Experimental Approach* Second Revised (2004) and Expanded Edition by Terence N. Mitchell, Burkhard Costisella.
- [19] Text book of *High resolution NMR techniques in organic chemistry*, vol 27, *tetrahedron organic chemistry series* (2004).
- [20] Text book of *Organic spectroscopy* by William Kemp.
- [21] Text book of *Spectroscopy of organic compounds* by P.S. Kalsi
- [22] Text book of *the vibrational spectroscopy of polymers*. D.I. Bower and W.F. Maddams.
- [23] Text book of *Structural identification of organic compounds with spectroscopic techniques* by Young-Cheng Ning (2005).