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Short Communication

FTIR Studies on Silver-Poly(Methylmethacrylate) Nanocomposites via *In-Situ* Polymerization Technique

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Silver-poly(methylmethacrylate) (Ag/PMMA) nanocomposites were prepared via in-situ polymerization technique using N,N'-dimethylformamide (DMF) as a medium. The Ag/PMMA was characterized by transmission electron microscopy (TEM) and Fourier transform infrared spectroscopy (FTIR). TEM images of the nanocomposites at 10% loading of Ag for 80°C revealed the presence of Ag/PMMA particles with an average diameter of 24 nm. When the concentration of Ag/PMMA solution increased, the ester carbonyl group stretching vibration, C=O peaks shifted to lower wavenumbers. At a higher temperature of 120 °C, the intensity of the solutions was 44% due to the increase of supplied heat to the sample.

Keywords: Fourier transforms infrared spectroscopy (FTIR); Polymer; In-situ polymerization technique; Transmission electron microscopy (TEM)

1. INTRODUCTION

Noble metal nanoparticles exhibit new physical-chemical properties which are not observed either in individual molecules, or in bulk metals [1 - 3]. For example, gold and silver nanoparticles exhibit strong absorption of electromagnetic waves in the visible range due to surface plasmon resonance (SPR). SPR is caused by collective oscillations of the conduction electrons of nanoparticles upon irradiation with visible light [4]. The SPR is highly influenced by the shape and size of nanoparticles. Notwithstanding the fact that as compares with gold particles, silver nanoparticles stabilized inappropriately undergo fast oxidation and easily aggregate in a solution, which complicates their use in the development of sensors and optical instruments. It also has an extensive range of applications such microelectronics [5], optical devices [6], catalysis [7] and drug delivery systems [8].

There are a several works on synthesis of Ag nanoparticles in such as with poly(vinylalcohol) (PVA) [3, 4, 9]. It has been reported that PVA is an excellent host polymer for silver and gold nanoparticles [9-10]. However, the stability of these particles in PVA has a limited shelf-life [9, 10]. The stability of Ag nanoparticles was improved in poly(vinylpyrolidone) (PVP) [9,11,12] and polystyrene (PS) [13] possibly due to the presence of free electrons in functional groups of the polymer chain which allow the particles to be held more firmly by the functional group of the polymer. This is turn results in enhanced stability of the particles. Earlier reports [14, 15] described the use of sodium salt containing acrylic acid for Ag nanoparticles in PMMA synthesized via radiolysis method. The reduction of Ag ions on polyacrylate chains were attributed to hydrated electrons or hydrogen.

Polymers are considered to be a good host material for metal and semiconductor nanoparticles, which exhibit exceptional optical and electrical properties. Nanoparticles significantly affect the polymer matrix due to their surface ratios, leading to new properties which are not present in either of the pure materials. Mulvaney [16] and Kelly et al. [17] stated that the incorporation of silver nanoparticles in a polymer matrix can significantly affect the properties of the matrix. In-situ polymerization has been proven to give significant improvement to the modification between inorganic particles and the polymer matrix [18].

The key to a successful synthesis of Ag/PMMA nanocomposites is to have a concealed PMMA polymerization in the surface of silver nanoparticles. A PMMA bi-in-situ forms an active site, which initiates concealed polymerization and gives rise to nano dispersion of Ag/PMMA nanocomposites. In this paper, poly(methylmethacrylate) (PMMA) acts as a protective agent and restricts the mobility of silver ions during the reaction, and hence, agglomeration is mostly controlled. Ag/PMMA nanocomposites were produced by in-situ polymerization technique without using any external chemical reagent. Dimethylformamide (DMF) was used as a solvent for chemical network between silver nanoparticles and PMMA.

2. EXPERIMENTAL

2.1 General

Silver nitrate, DMF and Daxad 19 were purchased from Fisher Scientific,UK, Qualigens, India and Canamara United, respectively. PMMA and PEG were purchased from Thermo Fisher Scientific, New Jersey, USA. Distilled water has been used in this work. The chemicals were employed without any further purification. In this work, IR spectroscopy was carried out using FTIR Perkin- Elmer Spectrum 400 within the wave region of 4000 to 500 cm^{-1} and a resolution of 4 cm^{-1}. The particle size and morphology were detected by LEO Libra® 120 Transmission Electron Microscopy operating at 120 kV.

2.2 Synthesis of silver/PMMA nanocomposites

10 g of PMMA was dissolved in 50 mL DMF. 5 mL of freshly prepared solutions of silver nanoparticles were added in such a way to obtain 10% loading of Ag nanoparticles in PMMA at 120

°C. The mixture was stirred for 1 h at room temperature in order to mature the reaction. This procedure was repeated for different amounts of PMMA and silver nanoparticles solutions to obtain 6% and 8% loading of Ag nanoparticles in PMMA at a temperature of 80 °C and 100 °C. When the stock solutions of silver nanoparticles and PMMA in DMF were stirred at room temperature, a golden yellow solution was obtained due to the formation of silver colloids, which consists of silver nanoparticles. A clear yellow to golden yellow solution was produced. The Ag/PMMA nanocomposites samples were characterized by TEM and FTIR techniques. The details of experiment procedure and conditions are summarized in Table 1.

Table 1. The preparation conditions of Ag/PMMA nanocomposites at various temperature and concentrations.

Reactant temperature (°C)	Reaction Time (h)	Adding time of PEG (min)	$AgNO_3$ (g)	Daxad 19 (g)	PEG (g)	PMMA (g)	Pure Ag (mL)
80~6%	1	10	2	3	4.5	6	3
80~8%	1	10	3	4	4.5	8	4
80~10%	1	10	4	5	4.5	10	5
100~6%	1	2 and 30	2	3	4.5	6	3
100~8%	1	2 and 30	3	4	4.5	8	4
100~10%	1	2 and 30	4	5	4.5	10	5
120~6%	1	5	2	3	4.5	6	3
120~8%	1	5	3	4	4.5	8	4
120~10%	1	5	4	5	4.5	10	5

3. RESULTS AND DISCUSSION

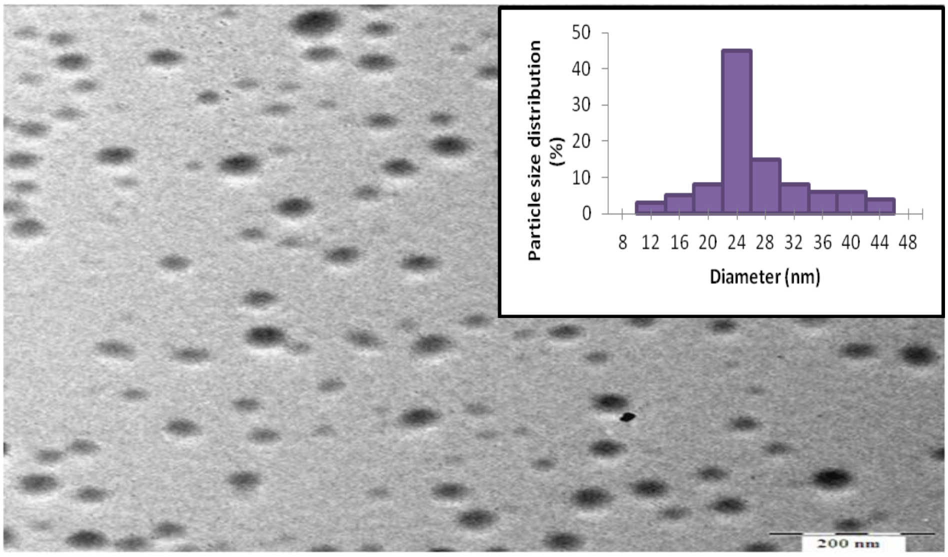

Figure 1. TEM image of Ag/PMMA nanocomposites for 10% laoding of Ag nanoparticles at 80 °C and particle size distribution (inset)

Fig. 1 shows the TEM image and particle size distribution of Ag/PMMA nanocomposites at 10 % loading of Ag nanoparticles for 80 °C. The presence of spherical Ag particles with an average diameter of about 24 nm is clearly observed. It is interesting to note that the silver nanoparticles are all obtained to be nanospherical shaped, well bounded and separated by a white layer adsorbed on the particle surfaces. This represents the presence of methyacrylate (MA). The atoms are arranged in an orderly manner, indicating that the aggregation process at this temperature may be in an equilibrium condition, which a slow reaction rate [19].

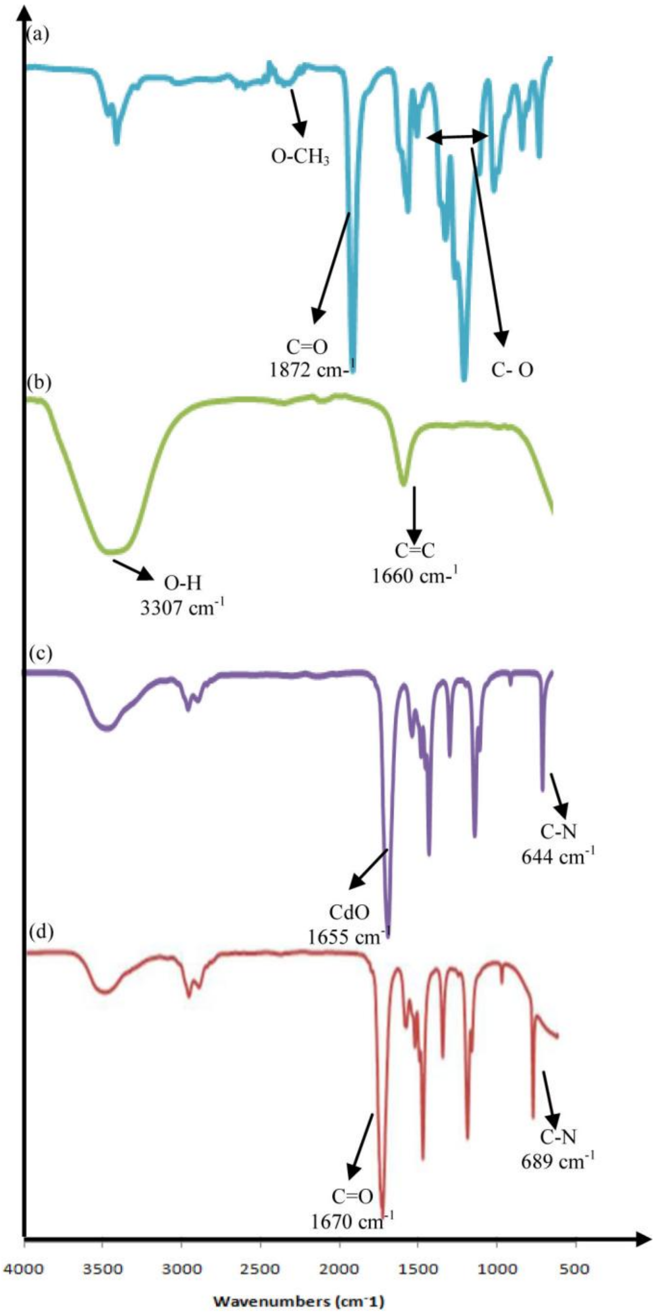

Figure 2. FTIR spectra of (a) PMMA (b) Ag nanoparticles (c) DMF (d) Ag/PMMA nanocomposites (120°C).

The FTIR spectra of Ag/PMMA nanocomposites at 120°C are shown in Fig. 2. The FTIR spectrum of PMMA in Fig. 2(a) indicates the details of functional groups present in the synthesized PMMA. A sharp intense peak appeared at 1872 cm^{-1} due to the presence of ester carbonyl group stretching vibration, C=O stretching [20]. The broad peak ranging from 1260-1000 cm^{-1} can be explained owing by the C-O (ester bond) stretching vibration. The broad peak ranging from 4000-2900 cm^{-1} is attributed to the presence of stretching vibration and a peak at 1195 cm^{-1} is assigned to –O-CH$_3$ stretching vibrations [21]. Fig. 2(b) shows the IR spectrum of silver nanoparticles. The peaks at 1660 and 3307 cm^{-1} are assigned to C=C stretching and O-H broadening stretching peak.

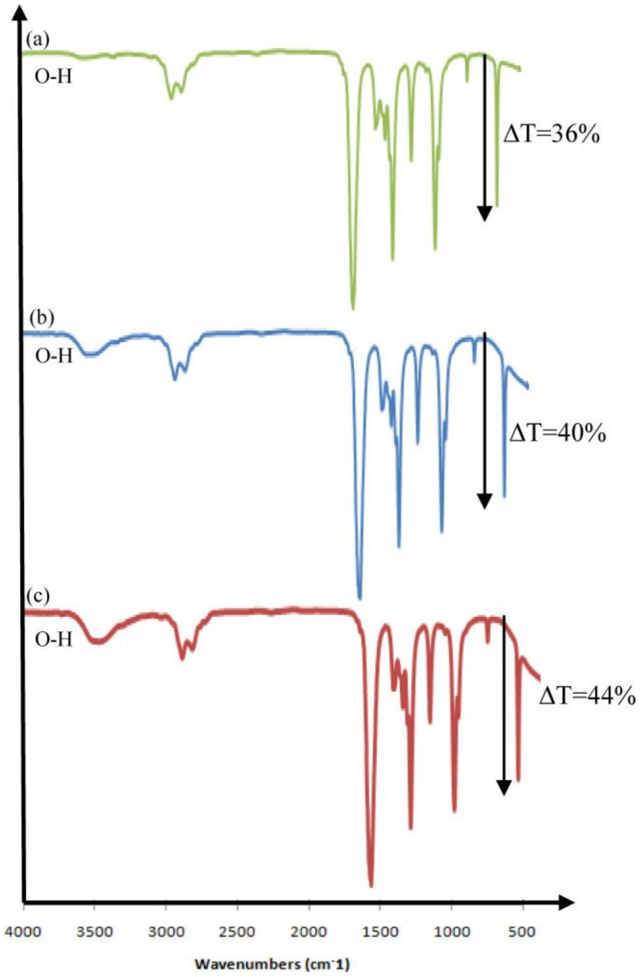

Figure 3. FTIR spectra of Ag/PMMA nanocomposites at different temperature (a) 80 °C (b) 100 °C (c) 120°C

The main bands of DMF in Ag/PMMA nanocomposites spectra are clearly seen in Fig. 2(c). The feature similarities in the FTIR spectra between DMF and Ag/PMMA nanocomposites verify the vital element of DMF in Ag/PMMA nanocomposites. It is found that CdO (~1655 cm$^{-1)}$ and C-N (~ 644 cm$^{-1)}$ vibration modes of DMF in Ag/PMMA nanocomposites are almost similar to those in the DMF solvent [22]. The band at 1655 cm^{-1} was shifted to 1670 cm^{-1} due to strength of CdO bond. The band at 644 cm^{-1} shifted to 689 cm^{-1}, which was possibly due to the increase in the order of the amide C-N bond [23-24].

Fig. 3 depicts the FTIR spectra of Ag/PMMA nanocomposites at different temperatures. The bands intensities slightly increase as the temperature increases. In the O-H region at ~ 3521 cm^{-1}, the full width at half maximum (FWHM) at 120°C is slightly wider than that at 80°C and 100°C. The increase in water content may originate from the environment or product of the chemical reaction. Fig. 4 illustrates the IR spectra of Ag/PMMA nanocomposites within the region of 1700 to 1300 cm^{-1} at 120°C for various concentrations of Ag. The interaction of the PMMA segments with silver nanoparticles is demonstrated to be dependent on the regimes of the adsorption of polymer chain onto the surfaces [25]. This interaction persuades the structural interphase alterations. It is clearly seen that as the concentration of the Ag/PMMA nanocomposites solution increases, the peaks shifted to lower wave numbers. The peak in Fig. 4(b) shifted about 2 cm^{-1} (to 1662 cm^{-1}) with respect to the peak at 1660 cm^{-1} observed in Fig. 4(c). The peak in Fig. 4(a) broadens at about 9 cm^{-1} (to 1669 cm^{-1}).

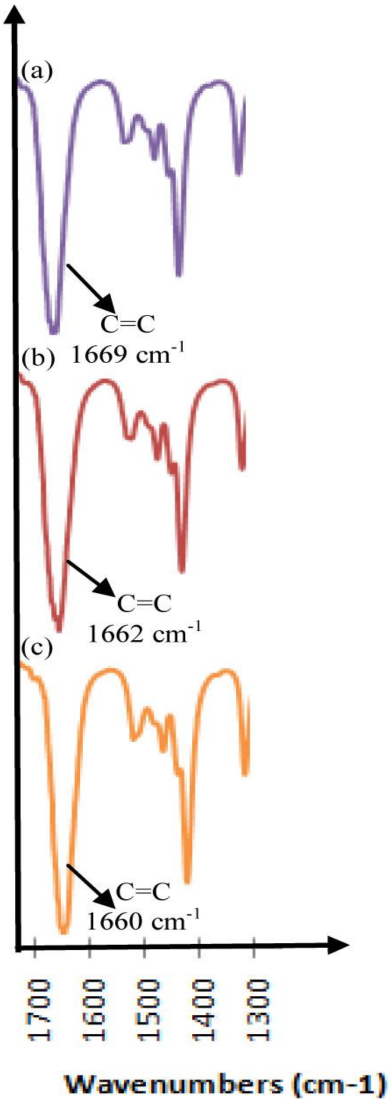

Figure 4. FTIR spectra of Ag/PMMA nanocomposites at various concentrations (Refer Table 1) (a) 120 °C ~ 6% (b) 120 °C ~ 8% (c) 120 °C ~ 10%

4. CONCLUSIONS

In this research, Ag/PMMA nanocomposites have been synthesized via by in-situ polymerization technique. A PMMA by in-situ polymerization technique forms an active site, which initiates concealed polymerization and gives rise to nano dispersion of Ag/PMMA nanocomposites. High-quality Ag/PMMA nanocomposites having spherical shape and narrow size distribution have been synthesized successfully. Increasing temperature and conceal by PMMA matrix forced the silver nanoparticles inside the matrix to transform into spherical shape. The mean particle diameter of Ag/PMMA nanocomposites showed an increasing trend with increasing temperatures at higher concentrations of silver nanoparticles suspension. The FTIR spectra confirm the complexation and interaction among the compounds. The interaction persuades the structural interphase alterations in the Ag/PMMA nanocomposites.

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References

1. R.M. Bruins, S. Kapil and S.W. Oehme, *Ecotoxicol Environ. Saf,* 45 (2000) 198–207.
2. T.J. Beveridge, M.N. Hughes, H. Lee, K.T. Leung, R.K. Poole, I. Savvaidis, S. Silver and J.T. Trevors, *Adv. Microb. Physiol*., 38 (1997) 178–243.
3. M. Sastry, A. Ahmad, M.I. Khan, R. Kumar, *Curr. Sci*. 85 (2003) 162–170.
4. J.D. Holmes, P.R. Smith, R. Evans-Gowing, D.J. Richardson, D.A. Russel, J.R. Arch. *Microbiol*. 163 (1995) 143–147.
5. Z. Zhang and M. Han, *J. Mater. Chem. Commun*. 13 (2003) 641.
6. A.V. Firth, S.W. Haggata, P.K. Khanna, S.J. Williams, J.W. Allen, S.W. Magennis, I.D.W. Samuel, D.J. Cole-Hamilton, *J. of Lumin*. 109, (2004) 163-172.
7. Y. Zhou, S.H. Yu, C.Y. Wang, X.G. Li, Y.R. Zhu, Z.Y. Chen, *Adv. Mater*. 11 (1999) 850-852.
8. K.-S. Chou, C.-Y. Ren, *Mater. Chem. Phys*. 64 (2000) 241.
9. P.K. Khanna, N. Singh, S. Charan, V.V.V. Subbarao, R. Gokhale, U.P. Mulik, *Mater. Chem. Phys.* 93 (2005) 117-121.
10. P.K. Khanna, R. Gokhale, V.V.V.S. Subbarao, A.K. Viswanath, B.K. Das, C.V.V. Satyanarayana, *Chem. Phys*. 92 (2005) 229-233.
11. Z. Zhang, B. Zhao, L. Hu, *J. Solid State Chem*. 121 (1996) 105-110.
12. R. He, X. Qian, J. Yin, Z. Zhu, *Chem. Phys. Lett*. 369 (2003) 454-458.
13. D. Wu, X. Ge, Y. Huang, Z. Zhang, Q. Ye, *Mater. Lett.* 57 (2003) 3549-3553.
14. Monti, O.L.A., Fourkas, J.T., Nesbitt, D.J., *J. Phys. Chem*. B 108 (2004) 1604-1612.
15. L. Longenberger, G. Mills, *J. Phys. Chem*. 99 (1995) 475-478.
16. Mulvaney, P., *Langmuir,* 12 (1996) 788
17. K.L. Kelly, E. Corondo, L.L. Zhou, G.C. Schatz, *J. Phys Chem* B., 107 (2003) 668
18. E. Marutani, S. Yamamoto, T. Ninjbagar, Y. Tsuji, T. Fukuda, M. Takano, *Polymer,* 45 (2004) 2231
19. Nurul Akmal Che Lah, Mohd Rafie Johan, *Applied Surface Science* 257 (2011) 7494–7500.
20. N. Singh and P.K. Khanna, *Mater. Chem. And Phys*.,104 (2007)367-372.
21. A. Balamurugan, S. Kannan, V. Selvaraj, S.Rajeswara, *Artif. Organs* 18 (2004) 41-45.

22. Pavia, D. L.; Lampman, G. M.; Kriz, G. S., Jr Introduction to Spectroscopy: A Guide for Students of Organic Chemistry; W. B. Saunders Co.: Philadelphia, PA, 1979.
23. Yilmaz, Y. T.; Topcu, Y. *Thermochim. Acta* 307 (1997) 143-147.
24. E.W. Randall, C.M.S. Yoder and J.J. Zuckerman. *Inorg. Chem*. 5 (1966) 1966.
25. Hershkovits, E., Tannenbaum,A., and Tannenbau. R., American *Chem. Soc., Mater*. 10 (2007) 21.