World Academy of Science, Engineering and Technology
International Journal of Materials and Metallurgical Engineering
Vol:4, No:4, 2010

Synthesis and Characterization of Silver/Polylactide Nanocomposites

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Open Science Index, Materials and Metallurgical Engineering Vol:4, No:4, 2010 publications.waset.org/11959/pdf

Abstract—Silver/polylactide nanocomposites (Ag/PLA-NCs) were synthesized via chemical reduction method in diphase solvent. Silver nitrate and sodium borohydride were used as a silver precursor and reducing agent in the polylactide (PLA). The properties of Ag/PLA-NCs were studied as a function of the weight percentages of silver nanoparticles (8, 16 and 32 wt% of Ag-NPs) relative to the weight of PLA. The Ag/PLA-NCs were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), electro-optical microscopy (EOM), UV-visible spectroscopy (UV-vis) and Fourier transform infrared spectroscopy (FT-IR). XRD patterns confirmed that Ag-NPs crystallographic planes were face centered cubic (fcc) type. TEM images showed that mean diameters of Ag-NPs were 3.30, 3.80 and 4.80 nm. Electro-optical microscopy revealed excellent dispersion and interaction between Ag-NPs and PLA films. The generation of silver nanoparticles was confirmed from the UV-visible spectra. FT-IR spectra showed that there were no significant differences between PLA and Ag/PLA-NCs films. The synthesized Ag/PLA-NCs were stable in organic solution over a long period of time without sign of precipitation.

Keywords—Nanocomposites, Polylactide, Silver Nanoparticles, Sodium Borohydride, Transmission Electron Microscopy.

I. Introduction

POLYMER biomaterials are usually employed, for medical implant and tissue engineering. These polymer biomaterials include poly (3-hydroxybutyrate) (PHB), poly (ϵ-caprolactone) (PCL), poly (glycolic acid) (PGA) and polylactide (PLA) [1], [2], [3], [4], [5]. For restoring and reconstructing defected medical tissue and implants, these biomaterials seem to be beneficial and promising. The following advantages are needed for having an optimal scaffold for medical applications: suitable for cell adhesion, greatly porous for transport of nutrients and metabolic waste, biodegradable and bioresorbable, proliferative. Furthermore, tissue engineering scaffolds needs to have antibacterial properties because of the risk of infection [6]. While treating of wound, infection is a common risk that must be prevented for a better healing of the wound. Silver and its compounds have been studied for many years not only for their antibacterial activity, but also for their low toxicity [7], [8], [9], [10], [11]. Polymers have been employed as stabilizer to provide stability for the noble metal nanoparticles against oxidation [12], or as matrices in nanocomposites, polymers have been used as stabilizers. In order to give discrete silver nanoparticles, studies of Ag-NPs in different polymers have been reported. The examples include the synthesis in polyvinylpyrrolidone (PVP), poly (vinyl alcohol), hyperbranched polyurethane (HP) and polyacrylonitrile (PAN) [13], [14], [15], [16]. Due to the different chemical structures and silver-polymer interactions, there is considerable variation of the average sizes and shapes of the silver nanoparticles produced. Natural polymers such as chitosan, PLA, and starch have received great attention due to their biocompatibility, biodegradability and non-toxic. PLA has an extensive medical application including surgical implants, restorable sutures, wound closure, and controlled release systems [17], [18], [19], [20]. For these reasons, PLA was chosen in this study for designing a composition of tissue engineering scaffold. To date, there has not been any report of study on PLA by chemical reducing methods, the polymer of interest in this research. Ag/PLA-NCs were prepared via chemical reduction method in diphase solvent using silver nitrate and sodium borohydride as a silver precursor and reducing agent, respectively.

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II. Experimental

All reagents in this work were of analytical grades and used as received without further purification.

A. Materials

Polylactide (PLA), was supplied by Nature Works 4060D, (USA), $AgNO_3$ (99.98%) and $NaBH_4$ (98.5%), obtained from Sigma-Aldrich (USA), N, N-Dimethyl Formamide (DMF, 99.0% and dichloromethane (CH_2Cl_2,99.0%) were purchased from Merck (Germany). All aqueous solutions were prepared using double distilled water.

B. Synthesis $Ag/PLA{-}NCs$

PLA was dissolved in a mixed solvent of DMF and CH_2Cl_2 (1/9 v/v) to achieve a concentration of 10 wt% and different amounts of $AgNO_3$ (0.8, 1.6 and 3.2g) were added to the solutions. The $AgNO_3$/PLA solution becomes colourless when stirred for 48 h in an ice water bath, and 10 ml of $NaBH_4$ aqueous solution (molar ratio of $AgNO_3/NaBH_4$ was 1:2) was added dropwise under vigorous stirring at the same temperature for 2h. The formation of the Ag-NPs started in the aqueous phase, but later the nanoparticles transferred

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to the organic phase due to the presence of van der Waals interactions between the hydroxyl groups of the PLA and the partial charged surrounded in the surface of the Ag-NPs [21], [22].The organic phase containing stable Ag-NPs colloid (8, 16 and 32 wt% respectively) relative weight of PLA was separated from aqueous phase and shaken with double-distilled water twice to remove any polar compound. After drying at room temperature, the Ag/PLA-NCs films were dissolved in CH_2Cl_2 and dried using solution-casting technique after ultrasonicated for 15 min.

C. Characterization

The synthesized of Ag/PLA-NCs were characterized using XRD, TEM, EOM, UV-vis and FT-IR. Meanwhile, the structure of the Ag/PLA-NCs was studied using the X-ray diffraction (XRD, Philips, X′pert, Cu Kα) at a scanning speed of 2%min. The TEM observations were carried out using Hitachi H-7100 electron microscope, and the particle size distributions were determined using the UTHSCSA Image Tool version 3.00 programme. Electro-optical microscopy (EOM) observations were carried out by Olympus BX51M microscope. The UV-vis spectra were recorded over the range of 300-700 nm with an H.UV 1650 PC-SHIMADZU B, UV-vis spectrophotometer. FT-IR spectra were recorded over the range of (400-4000) cm^{-1} with a Perkin Elmer 1650, FT-IR spectrophotometer.

III. Results and Discution

A. X-ray diffraction

The XRD patterns of PLA and Ag/PLA-NCs are shown in Figure 1. In addition to the broad diffraction peak centered at 16.25 which can be assigned to PLA, five crystalline peaks are observed at the 2θ of 38.18, 44.30, 64.55,77.54 and 81.71. They are attributed to the (111), (200), (220), (311) and (222) crystallographic planes of face-centered cubic (fcc) silver crystals, respectively (XRD Ref. No. 01-087-0718) [23]. The XRD peak broadenings of Ag-NPs are mostly due to the presence of nano-sized particles in the nanocomposites [24]. The silver crystalline peak intensities also increase with the increase in the percentage of Ag-NPs in PLA, which implies that the Ag-NPs are embedded in the PLA.

B. UV-visible spectroscopy

After the addition of reducing agent, the colour of the solution ($AgNO_3$/PLA) turned light brown, brown and dark brown for 8, 16 and 32wt% of Ag-NPs respectively (Figure 2a-b). The generation of Ag-NPs can be identified from the UV-vis spectra (Figure 3) where the characteristic of the silver surface plasmon resonance (SPR) bands are found at around 400 nm. These absorption bands are presumably corresponding to the Ag-NPs smaller than 10 nm [25], [26]. Nonetheless, there is no characteristic UV-vis absorption of Ag-NPs before the addition of $NaBH_4$ into PLA/$AgNO_3$ (Figure 3a), while the growth of the plasmon peak at 433 nm indicates the formation of Ag-NPs (Figure 3b). The absorption peaks for the 16 and 32 wt% of Ag-NPs (Figure 3c-d) are slightly shifted to the lower wavelength (424 nm) indicating that mean diameters of Ag-NPs have increased [27].

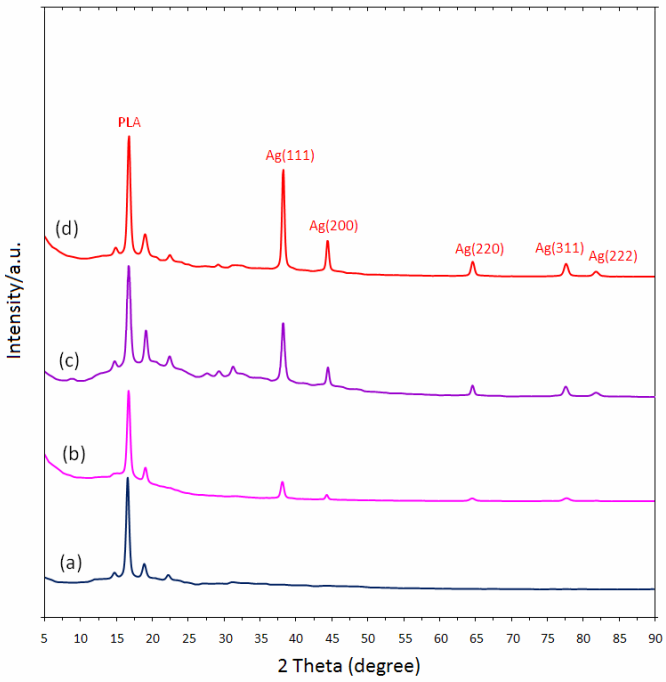


Fig. 1. XRD patterns of PLA (a), Ag/PLA-NCs at 8 (b), 16 (c), 32 (d) wt% Ag-NPs.

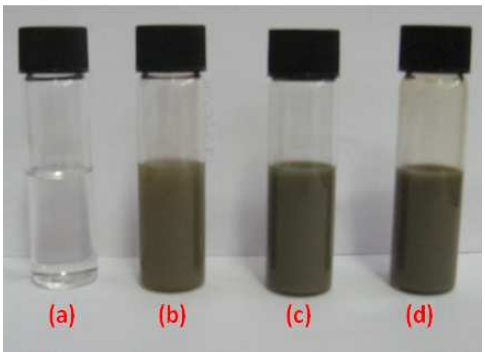


Fig. 2. Photograph of AgNO3/PLA (a), Ag/PLA-NCs at 8 (b), 16 (c), 32 (d) wt% Ag-NPs.

C. Morphology

Figure 4 illustrates the TEM, size distribution and EOM images of Ag/PLA-NCs films containing different amounts of Ag-NPs. TEM image and their size distribution show that the mean diameters and standard deviation of Ag-NPs (8, 16 and 32 wt% relative to PLA) are 3.30±0.78, 3.80±0.85 and 4.80±1.15 nm respectively. Furthermore, this confirms the uniform distribution of the Ag-NPs in the PLA matrix, although particles seem to aggregate to some extent. The observation could be attributed to a strong interaction between Ag-NPs and PLA molecular chains, which promoted phase separation of polymer, thus preventing Ag-NPs from coagulating in the reduction process. TEM images show that with the increased percentages of Ag-NPs in the polymeric matrix, particle diameters and standard deviation are increased. Meanwhile, EOM confirmed that with increasing Ag-NPs percentage in PLA, external surfaces of polymers become

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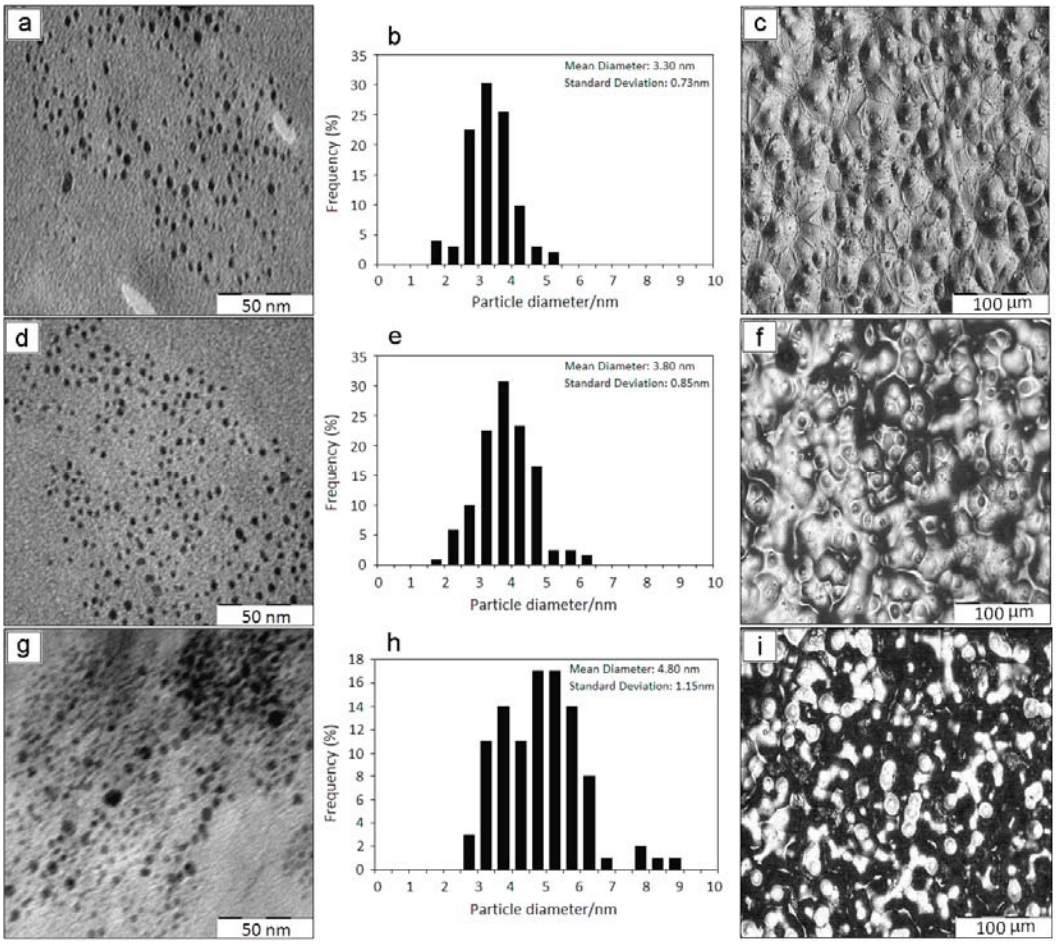


Fig. 4. TEM images, their corresponding size distributions and EOM images of Ag/PLA-NCs at different wt% of Ag-NPs; 8 (a-c), 16 (d-f) and 32 (g-i).

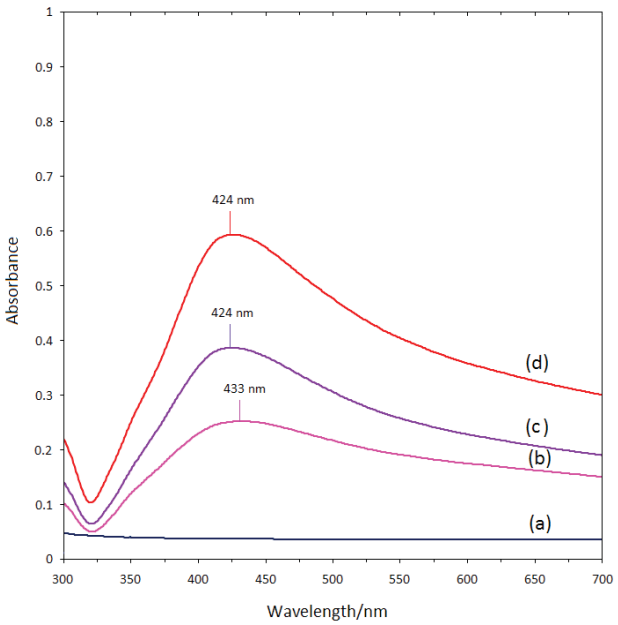


Fig. 3. UV-visible spectra of PLA (a), Ag/PLA-NCs at 8 (b), 16 (c), 32 (d) wt% Ag-NPs.

spherulitic morphology and more shining.

D. FT-IR analysis

FT-IR spectroscopy was used to characterize the interaction between the Ag-NPs with PLA. Figure 5 shows FT-IR peaks for PLA and *Ag/PLA-NCs* (8, 16, and 32 wt% relative to PLA). The peaks at 1177 (1071), 2989 (2936) and 3502 cm^{-1} were assigned to the C−O, C−H (double) and O−H stretching of the $-CH(CH_3)-OH$ end group of PLA, respectively. The splitting of the C=O carbonyl stretching at ca. 1744 cm^{-1} might be due to the presence of −CH−CO−O− group. The peaks at 1448, and 1356 cm^{-1} were assigned $-CH_3$, and −CH− bending including symmetric and asymmetric, bending [28], [29]. The interactions between PLA chain molecules and Ag-NPs are associated with the peak at 3493 cm^{-1}. Broad peak is due to the presence of van der Waals interactions between the hydroxyl groups of PLA and the partial positive charge on the surface the Ag-NPs [30].

IV. Conclusion

A simple way to prepare uniform size of Ag-NPs in PLA by reacting different percentages of nanoparticles in PLA with sodium borohydride as reducing agent was developed.

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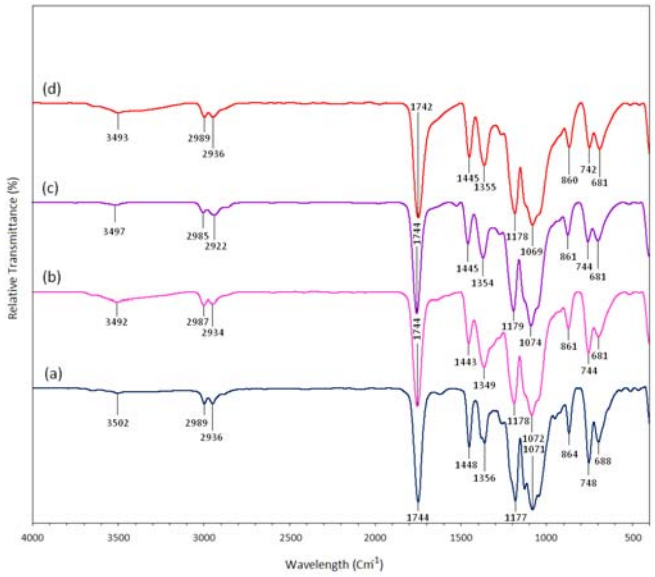


Fig. 5. FT-IR spectra of PLA (a), Ag/PLA-NCs at 8 (b), 16 (c), 32 (d) wt% Ag-NPs.

The average diameters of the Ag-NPs are between 3.30, 3.80 and 4.80 nm with well-crystallized structures, and Ag-NPs diameters increase with increasing amount of $AgNO_3$ added. XRD analysis confirms that crystallographic planes of the silver crystal are the face-centered cubic (fcc) types. UV-vis absorption spectra show peaks characteristic of the surface plasmon resonance of Ag-NPs. FT-IR shows that interactions exist between molecules of PLA and Ag-NPs. The synthesized Ag/PLA-NCs colloids in the organic solvent were stable over a long period of time without any sign of precipitation.

Acknowledgment

Thanks are due to Mrs. Parvaneh Shabanzadeh for helpful discussion and ideas. The authors are also grateful to Mrs. A. Jusoh of TEM Unit of Institute of Bioscience UPM for technical assistance.

References

[1] Y. Chen, A. F. T. Mak, M. Wang, J. Li, M. S. Wong, *PLLA scaffolds with biomimetic apatite coating and biomimetic apatite/collagen composite coating to enhance osteoblastlike cells attachment and activity*, Surface and Coatings Technology, 201, 575-580, 2006.

[2] K. Tomihata, Y. Ikada, *In vitro and in vivo degradation of films of chitin and its deacetylated derivatives*, Biomaterials, 18, 567-575, 1997.

[3] D. H. Reneker, I. Chun, *Nanometre diameter fibres of polymer, produced by electrospinning*, Nanotechnology, 7, 216-223, 1996.

[4] V. J. Chen, P. X. Ma, *The effect of surface area on the degradation rate of nano-fibrous poly (L-lactic acid) foams*, Biomaterials, 27, 3708-3715, 2006.

[5] W. J. Li, R. Tuli, X. Huang, P. Laquerriere , R. S. Tuan, *Multilineage differentiation of human mesenchymal stem cells in a three-dimensional nanofibrous scaffold*, Biomaterials, 26, 5158-5166, 2005.

[6] X. Chen , H. J. Schluesener, *Nanosilver: a nanoproduct in medical application*, Toxicology Letters, 176, 1-12, 2008.

[7] F. Furno, K. S. Morley, B. Wong, *Silver nanoparticles and polymeric medical devices: a new approach to prevention of infection*, Journal of Antimicrobial Chemotherapy, 54, 1019-1024, 2004.

[8] D. K. Riley, D.C. Classen, L. E. Stevens, J. P. Burke, *A large randomized clinical trial of a silver-impregnated urinary catheter: lack of efficacy and staphylococcal superinfection*, The American Journal of Medicine, 98, 349-356, 1995.

[9] J. H. Crabtree, R. J. Burchette, R. A. Siddiqi, I. T. Huen, L. L. Hadnott, D. A. Fishman, *The efficacy of silver-ion implanted catheters in reducing peritoneal dialysis-related infections*, Peritoneal Dialysis International, 23, 368-374, 2003.

[10] B. Shan, Y. Z. Cai, J. D. Brooks, H. Corke, *Antibacterial properties of Polygonum cuspidatum roots and their major bioactive constituents*, Food Chemistry, 109, 530-537, 2008.

[11] V. Alt, T. Bechert, P. Steinrucke, *An in vitro assessment of the antibacterial properties and cytotoxicity of nanoparticulate silver bone cement*, Biomaterials, 25, 4383-4391, 2004.

[12] M. Rong, M. Zhang, H. Liu, H. Zheng, *Synthesis of silver nanoparticles and their self organization behavior in epoxy resin*, Polymer, 40, 6169-6178, 1999.

[13] M. Zheng, M. Gu, Y. Jin , G. Jin, *Optical properties of silver dispersed PVP thin film*, Materials Research Bulletin, 36, 853-859, 2001.

[14] P. K. Khanna, N. Singh, S. Charan, V. V. V. S. Subbarao, R. Gokhale, U. P. Mulik, *Synthesis and characterization of Ag/PVA nanocomposites by chemical reduction method* Materials Chemistry and Physics, 93, 117-121, 2005.

[15] H. W. Lu, S. H. Liu, X. L. Wang, X. F. Qian, J.Yin, Z. K. Zhu, *Silver nanocrystals by hyperbranched polyurethane-assisted photochemical reduction of Ag+*, Materials Chemistry and Physics, 81, 104-107, 2003.

[16] Z. Zhang, L. Zhang, S. Wang, W. Chen, Y. Lei, *A convenient route to polyacrylonitrile/silver nanoparticle composite by simultaneous polymerization-reduction approach* Polymer, 42, 8315-8318, 2001.

[17] R. A. Jain, *The manufacturing techniques of various drug loaded biodegradable poly (lactide-co-glycolide) (PLGA) devices*, Biomaterials, 2, 2475-2490, 2000.

[18] A. Mikos, M. Lyman, L. Freed, R. Langer, *Wetting of poly (L-lactic acid) and poly (D, L-lactic-co-glycolic acid) foams for tissue culture*, Biomaterials, 15, 55-58, 1994.

[19] M. S. Taylor, A. U. Daniels, K. P. Andriano, J. Six. Heller, *Bioabsorbable polymers: In vitro acute toxicity of accumulated degradation products*, Journal of Applied Biomaterials, 5, 151-157, 1994.

[20] T. Park, S. Cohen, R. Langer, *Poly (L-lactic acid)/pluronic blends: Characterization of phase separation behavior, degradation, morphology and as protein releasing matrices*, macromolecules, 25, 116-122, 1992.

[21] J. Turkevich, P. C. Stevenson, J. Hillier, *The nucleation and growth processes in the synthesis of colloidal gold*, Discussions of the Faraday Society, 11, 55-75, 1951.

[22] A. Roucoux, J. Schulz, H. Patin, *Reduced transition metal colloids: a novel family of reusable catalysts*, Chemical Reviews, 102, 3757-3778, 2002.

[23] M. K. Temgire, S. S. Joshi, *Optical and structural studies of silver nanoparticles*, Radiation Physics and Chemistry, 71, 1039-1044, 2004.

[24] V. Prasad, C. D. Souza, D. Yadav, A. J. Shaikh, N. Vigneshwaran, *Spectroscopic characterization of zinc oxide nanorods synthesized by solid-state reaction*, Spectrochimica Acta Part A. Molecular and Bimolecular Spectroscopy, 65, 173-178, 2006.

[25] N. Aihara, K. Torigoe, K. Esumi, *Preparation and characterization of gold and silver nanoparticles in layered laponite suspensions*, Langmuir, 14, 4945-4949, 1998.

[26] X. Z. Lin, X. Teng, H. Yang, *Direct synthesis of narrowly dispersed silver nanoparticles using a single-source precursor*, Langmuir, 19, 10081-10085, 2003.

[27] J. Lerme, B. Palpant, B. Pevel, M. Pellarin, M. Treilleux, J. L. Vialle, A. Perez, M. Broger, *Quenching of the size effects in free and matrix-embedded silver clusters*, Physical Review Letters, 80, 5105-5108, 1998.

[28] H. Younes, D. Cohn, *Phase separation in poly (ethylene glycol)/poly (lactic acid) blends*, European Polymer Journal, 24, 765-773, 1988.

[29] M. Agarwal, K. W. Koelling, J. J. Chalmers, *Characterization of the degradation of poly- lactic acid in a well-controlled composting system* Biotechnology Progress, 14, 517-526, 1998.

[30] E. C. Da silva, M. G. A. Da silva, S. M. P. Meneghetti, G. Machado, M. A. R. C. Alencar, J. M. Hickmann, M. R. Meneghetti, *Synthesis of colloids based on gold nanoparticles dispersed in castor oil*, Journal of nanoparticle research, 10, 201-208, 2008.



Mansor Ahmad (Assoc. Prof., Dr.) received the BSc.(1979) (Hons) in Chemistery from Indiana University, Bloomington, USA and MSc degrees (1982) from University of Kentucky, Lexington, USA and he received the PhD degree in (1994) University of Salford, UK. He is Associate Professor of the Department of Chemistry in University Putra Malaysia. He held didactic activity both undergraduate and post graduate level. He interest focuses synthesis and characterization of copolymeric hydrogels. Copolymers are prepared from hydrophilic monomers, such as N-vinyl-2-pyrrolidone (VP) and 2-hydroxyethyl methacrylate (HEMA), in combination with hydrophobic monomers. Characterization methods include common techniques such as thermal analysis, stress-strain measurements and water content determination. The states of water in hydrogels are determined by Differential Scanning Calorimetry (DSC). These hydrogels are used as matrices for controlled-release of bioactive chemicals and for immobilization of enzymes. He is also involved in the preparation of biodegradable plastics from indigenous starches. This project is being carried out in an effort to diversified the use of starch and to formulate an environmental-friendly packaging materials. In addition, Mansor is also interested in analytical chemistry, mainly on Thermal analysis and Nuclear Magnetic Resonance spectroscopy (NMR) studies on polymeric systems.

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