A novel approach to prepare poly (methyl methacrylate)/Ag nanocomposites

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ABSTRACT

Silver nanoparticles (AgNPs) were synthesized by novel and direct method throughout the *in situ* emulsion polymerization of MMA monomer to give poly (methyl methacrylate)/silver (PMMA/Ag) nanocomposites using different concentrations of silver nitrate ($AgNO_3$) solutions. The fashioned PMMA/Ag nanocomposites were characterized using UV spectroscopy, FT-IR spectroscopy. The structural and morphology of PMMA/Ag nanocomposites were characterized using X-ray diffraction pattern (XRD), as well as scanning electron microscope (SEM) and transmission electron microscope (TEM). Moreover, the prepared PMMA/Ag nanocomposites may be used as food packaging materials.
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INTRODUCTION

The polymer nanocomposites have attracted enormous attention lately owing to their advantageous in mechanical, optical properties and their thermal stability[1,2], which are mainly attributed to the high degree dispersion of layered inorganic compounds in the polymer matrix[3]. Among the polymer nanocomposites, exfoliated types of these materials frequently have molecular dispersion of high aspect ratio of inorganic layers in polymer nanocomposites[4]. There are many methods have been reported for the synthesis of exfoliated nanocomposites with good properties[5-7]. The favorable physical and chemical properties of inorganic and inorganic-organic[8] hybrid nanocomposites have recently provoked many laboratories to study these materials. The most frequently monomer is the methyl meth-

acrylate (MMA) which have been used in the preparation of nanocomposites water based polymerization reactions[9].

Inorganic antibacterial material is usually in the form of a nanocomposite is considered as highly safe materials due to (non-volatile) and heat resistant compared to organic materials. In addition; metallic ions having antibacterial and antifungal capabilities, such as silver, copper and zinc, are impregnated in a mineral or blended with a carrier to form the nanocomposites[10] or applied as a coating. Appropriate release of antibacterial metallic ions from the nanocomposites can effectively inhibit the birth and growth of harmful microbes. As Ag ions are taken into microbes, they react and bond to the cellular enzyme microbes this inhibits enzyme activity and multiplication of microbes, thus killing the microbes. When silver nanoparticles are incorporated into the poly-

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mer matrix, the prepared polymer nanocomposites become act as antibacterial materials[11].

Commonly, polymer nanocomposites containing nanometal were prepared in situ methods. The metal ions were reduced to nanoclusters inside polymer solution or prepolymer solution that could interpret to polymer afterward; in this case, nanometal particles would congregate in the polymer matrix because polymerization and reduction occurred separately. Until now, some typical methods include irradiation technique such as ultraviolet[12], γ-ray[13], microwave[14], ultrasound[15,16], and rapidly were developed to carry out bi-in situ synthetic technique. Ag nanoparticles nanocomposites have been reported in recent years[17-19], such as preparation, characterization, and application of polymer/silver nanocomposites, however, no reference on preparation of polymer/Ag nanocomposites prepared via in- situ emulsion polymerization technique. In present work an easy one-step synthetic way for PMMA/Ag nanocomposites with Ag nanoparticles as core and PMMA as shell by preparing Ag nanoparticles by reduction of Ag^+ to Ag^0 through C=O of methyl methacrylate.

MATERIALS AND METHODS

Materials

Methyl methacrylate (MMA) monomer, a product of schuchardt (yield 99%) stabilized with 14 ppm hydroquinone. It was purified by washing with a small amount of sodium hydroxide solution (5%), the MMA was separated with separating funnel and dried over anhydrous sodium sulphate. High purity silver nitrate ($AgNO_3$) was purchased from the No. 1 Chemical Reagent Company in Shanghai. Cetyltrimethyl ammonium bromide (CTAB) was provided by Merck, Darmstadt, Germany. Potassium persulphate (PPS) was used as received from Alfa Aesar.

Preparation of PMMA/Ag nanocomposites

The mixture containing silver nitrate, polymerizable monomer MMA, emulsifier, and distilled water, the emulsion polymerization process was carried out in a round bottomed two necked, Q.F. (250 ml) flask equipped with a mechanical stirrer, reflux condenser, and a thermometer. The polymerization was start by

dissolving persulphate (PPS) in aqueous phase (water) and the required amounts of silver nitrate ($AgNO_3$) was added to the monomer phase (0.0, 0.5, and 1.5 wt. %), then the mixture was dispersed in the aqueous phase and the polymerization was carried out under stirring at the required temperature (80°C), with stirring rate 500 r.p.m, for 8h. The brown emulsion was obtained by after certain minutes. The resultant emulsion was demulsified with anhydrous sodium sulfate, washed with absolute ethyl alcohol, and cleaned repeatedly with distilled water, and the brown powder was obtained. Finally, the products were subjected to vacuum drying at 75°C for 24 h for subsequent characterizations.

Characterization of PMMA/Ag nanocomposites

The XRD patterns investigations of the polymer nanocomposites were carried out on a Diano X-ray diffractometer using CoKá radiation source energized at 45 kV and a Philips X-ray diffractometer (PW 1930 generator, PW 1820 goniometer) with CuK radiation source (λ=0.15418 nm). The basal spacing (dL) was calculated from the (001) reflection via the Bragg,s equation. UV-Spectroscopy was carried by Shimadzu UV-Visible recording spectrophotometer UV-240. The thermal stability was studied using a Perkin Elmer Thermogravimetric analyzer (TGA), with a heating rate of 10°C/min in nitrogen atmosphere. Scanning electron micrographs (SEM) were taken using a FEI IN-SPECTS Company, Philips, Holland environmental scanning without coating. The nanostructure of sliver nanoparticles was elucidated by JEOL JEM-1230 transmission electron microscope (TEM) with acceleration voltage of 80 kV. The microscopy probes of the sliver nanoparticles was prepared by adding a small drop of the water dispersions onto a Lacey carbon film-coated copper grid then allowing them to dry in air.

RESULTS AND DISCUSSION

X-ray diffraction pattern (XRD) study

The emulsion polymerization of MMA monomer was carried out in presence of different concentration of $AgNO_3$ (0.5 and 1.5 wt %) depend on monomer amount which still constant at 9.5 wt % (10 ml). The three PMMA/Ag nanocomposites samples its crystal phase structure was characterized by XRD as shown
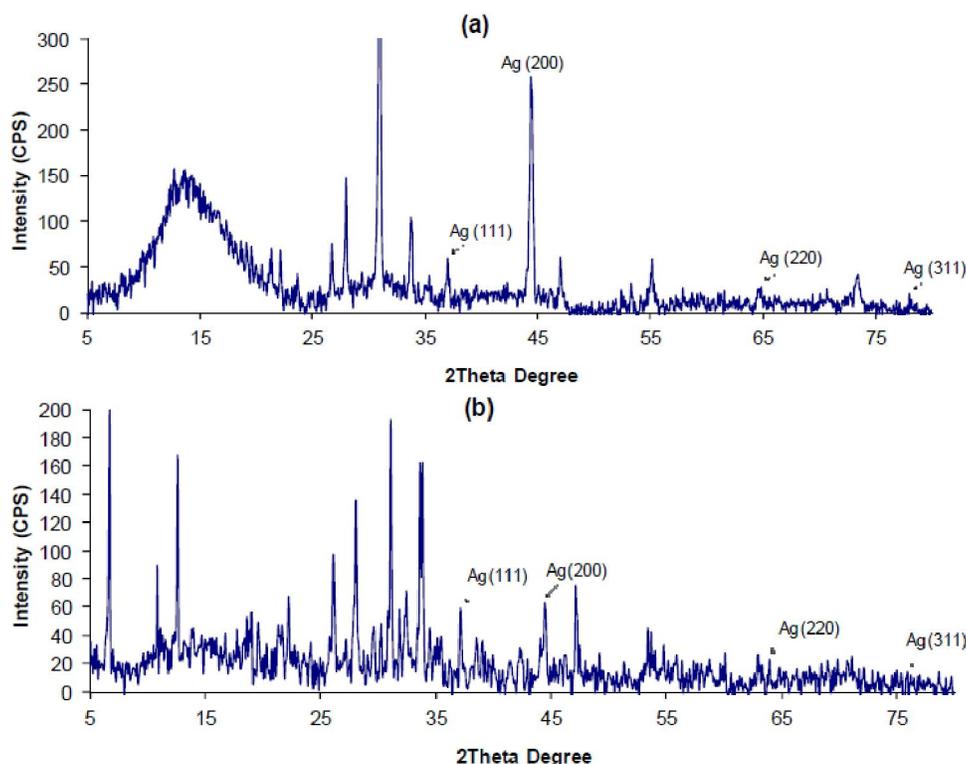
Figure 1 : XRD of PMMA/Ag nanocomposites prepared by in situ emulsion polymerization in presence of silver nitrate (AgNO₃) (a) 0.5 wt. %, (b) 1.5 wt. %.

in Figure 1. In the case, the PMMA/Ag nanocomposites exhibit five peaks, the wide diffraction peak at around 15 was derived from noncrystal PMMA. The other four peaks at 38, 44, 64, and 77 are characteristic diffraction peaks of metallic silver, corresponding to the four diffraction planes (111), (200), (220), and (311), respectively. But, based on asymmetry of the peak shape of 44.37, it was deliberation that there was a certain of abnormality at the face of silver phase (200), which was possibly related to PMMA chain grated on face of the silver nanoparticles crystal.

Infrared (IR) characterization of PMMA/Ag nanocomposites

The IR spectrum of nanocomposites was collected after purification and pellet pressed together with potassium bromide; the spectrum is presented in Figure 2. The characteristic peak of C=C (1638 cm^{-1}) which indicated the polymerization of MMA monomer occurred nearly completely disappeared in PMMA/Ag nanocomposites spectrum. Also, the characteristic peak of C=O (1734cm^{-1}) and of C–H (1438 cm^{-1}) in MMA spectrum were shifted to 1729 and 1465cm^{-1}, respectively in PMMA/Ag nanocomposites spectrum, and the

intensity of the two peaks was relatively improved, which implied that there existed interaction between silver nanoparticles and polymer matrix to some degree. Also, the three spectra of the prepared PMMA/Ag nanocomposites with different loadings of Ag nanoparticles approximately match and the difference appeared only in the intensity of the peaks.

Morphological study

The structure of the prepared PMMA/Ag nanocomposites was investigated in details by using scanning electron microscope (SEM) as well transmission electron microscope (TEM). A scanning electron microscope was employed to analyze the structure of the nanoparticles that were dispersed in nanocomposites. Figure 3 a displayed the formation of Ag nanoparticles with particle size ranging from 8-30 nm. Furthermore, the surface morphological properties of the prepared PMMA/Ag nanocomposites were examined and illustrated in (Figure 3b and c) since the percolation threshold in nanocomposites is related to the homogeneity of the mixing nanoparticles and polymer matrix in the prepared nanocomposites which containing different concentration of Ag nanoparticles. This

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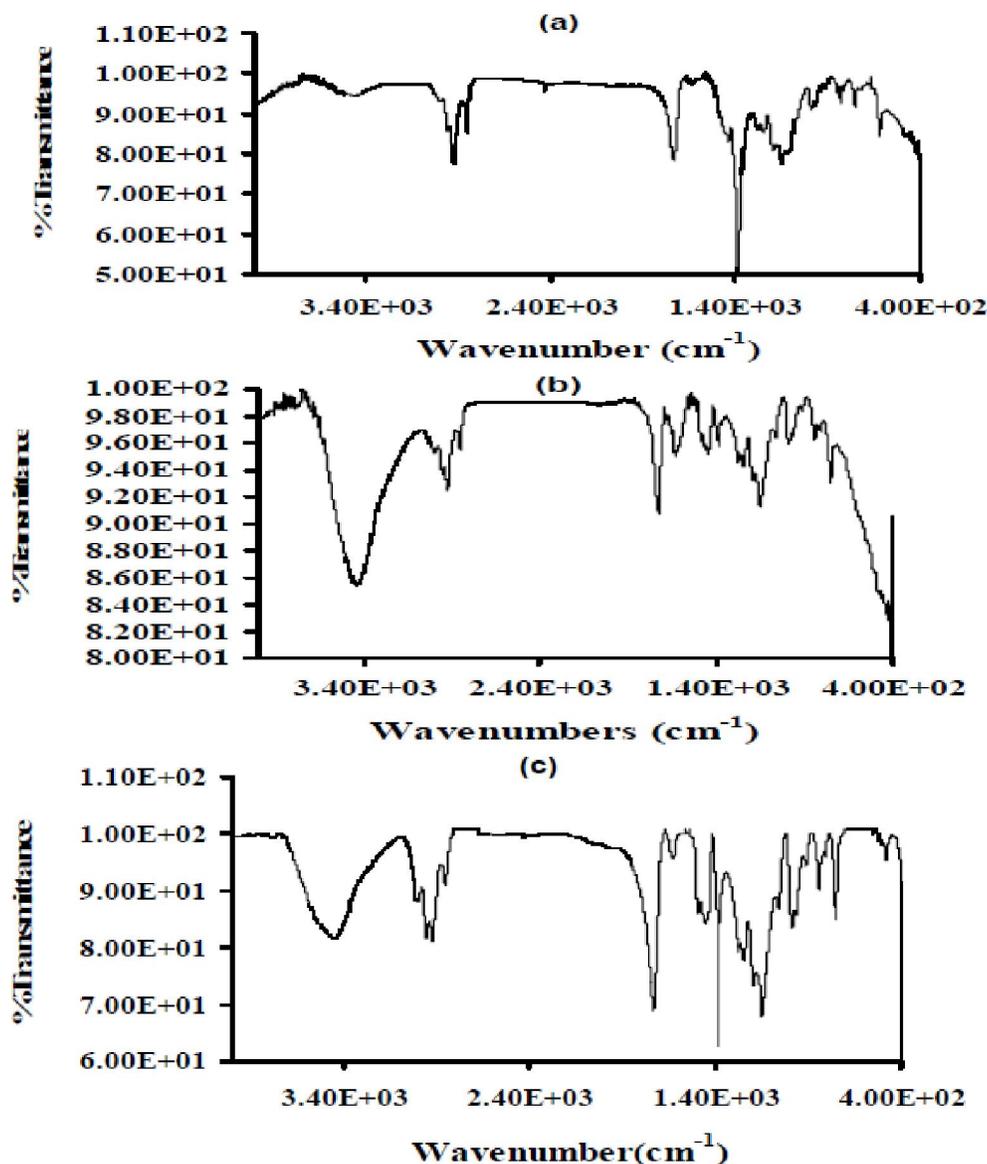
Figure 2 : Infrared spectra of PMMA prepared by emulsion polymerization in absences of AgNO$_3$ (a)as well as, PMMA/Ag nanocomposites prepared by in situ emulsion polymerization in presence of silver nitrate (AgNO$_3$) with different concentrations, (b) 0.5 wt. %, (c) 1.5 wt. %.

interaction may be accessible a large available surface area of the polymer matrix for chemical and physical interactions and antimicrobial activity.

The SEM results when suitably interpreted and combined with TEM results offer much information about the morphological structures of the Ag nanoparticles as well as the structure of the prepared PMMA/Ag nanocomposites. Complementary, these two techniques give evidence to help us to obtain significant relationships between the PMMA/Ag nanocomposites. Moreover, based on the obtained morphological data using transmission electron microscope (TEM) Figure 4a demonstrated the formation of silver nanoparticles when emulsion polymerization of MMA monomer carried out in presence of silver nitrate solution. Also, Figure 4b and c represent the PMMA/Ag nanocomposites which maintain the homogeneity and uniformity of the distribution of Ag nanoparticles on the surface of the prepared PMMA sheet when loading low concentration of silver nitrate (0.5 wt%) during emulsion polymerization of MMA monomer. While with increasing the loading of silver nitrate (1.5 wt %) the dispersion of Ag nanoparticles in PMMA matrix fashioned less homogeneity of the prepared nanocomposites, this owing to he agglomerate of silver nanoparticles in PMMA matrix due to its high surface area of Ag nanoparticles
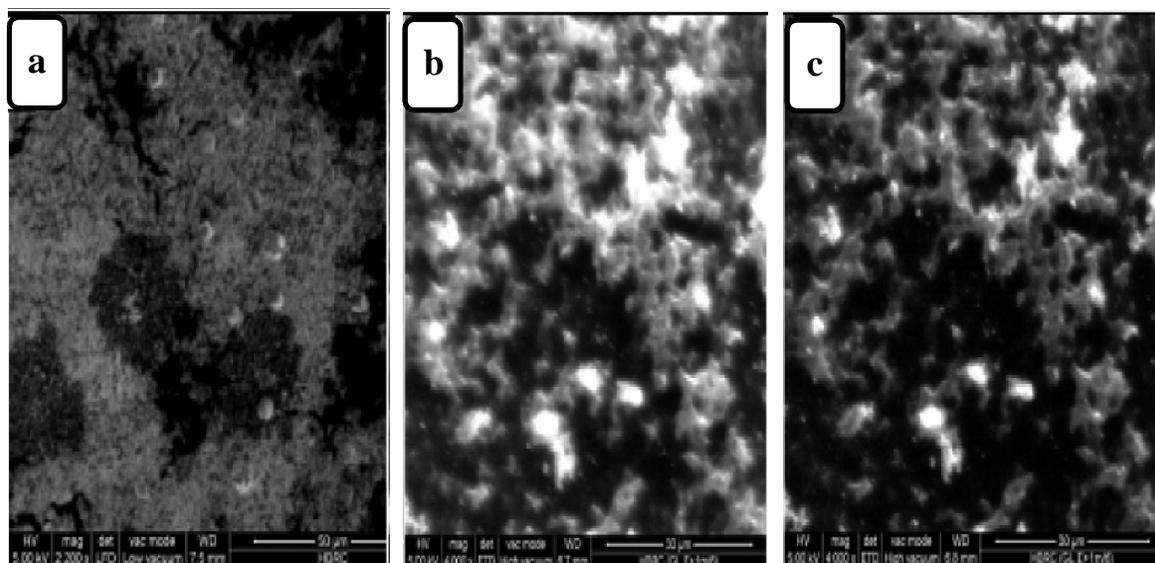
Figure 3 : SEM image of Ag nanoparticles (a) as well as PMMA/Ag nanocomposites with different concentrations (b) 0.5 wt %, (c) 1.5 wt %.
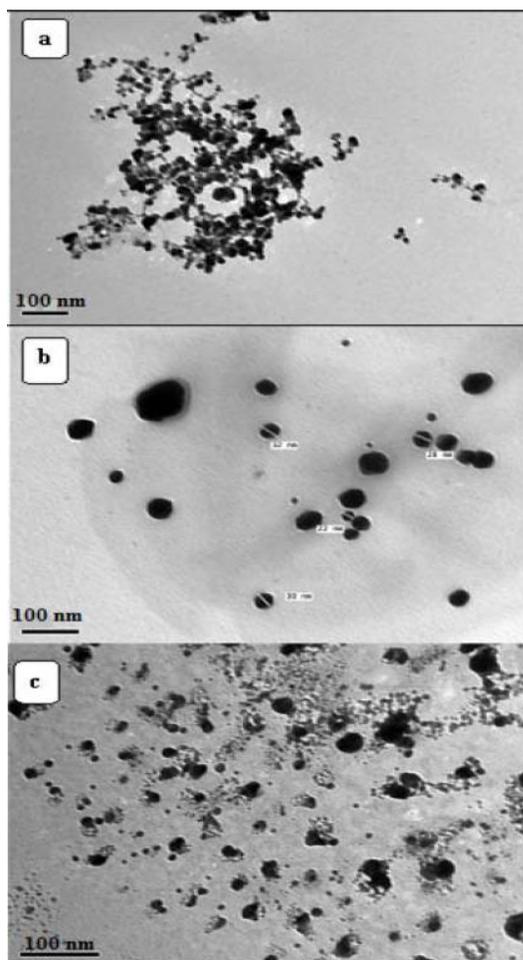
Figure 4 : TEM image of Silver nanoparticles (a) as well as PMMA/Ag nanocomposites containing different concentrations of Ag NPs (0.5 wt. % and 1.5 wt. % respectively, b, c).

Thermal stability of PMMA/Ag nanocomposites

The thermal stability of the prepared PMMA/Ag nanocomposites can be monitored by TGA, and the behavior is shown in (Figure 5) for pure PMMA and the prepared PMMA/Ag nanocomposites. It was reported that two main reaction stages happen through degradation of PMMA in nitrogen atmosphere[20]. The first stage, which can be divided into two steps, represents decomposition of weak head-to-head linkages and impurities for the range between 160 and 240°C, and decomposition of PMMA chain-ends around 290°C. The second stage, between 300 and 400°C, represents random scission of the polymer chains. In Figure 5a, the pure PMMA decomposition demonstrates two reaction stages, whereas the PMMA/Ag nanocomposites display only the second stage indicating random scission decomposition. PMMA/Ag nanocomposites showed enhanced thermal stability when compared to the pure polymer and increasing the thermal stability with increasing the Ag nanoparticles into PMMA matrix. This designates that the bound polymer chains near Ag nanoparticles might have higher thermal stability or may be affords a barrier which prevents release of evolved degradation products, they trapping the products which recombine to form thermally stable residues. Since, this enhancement in thermal stability of the prepared PMMA/Ag nanocomposites makes it as suitable material for packaging applications[21].

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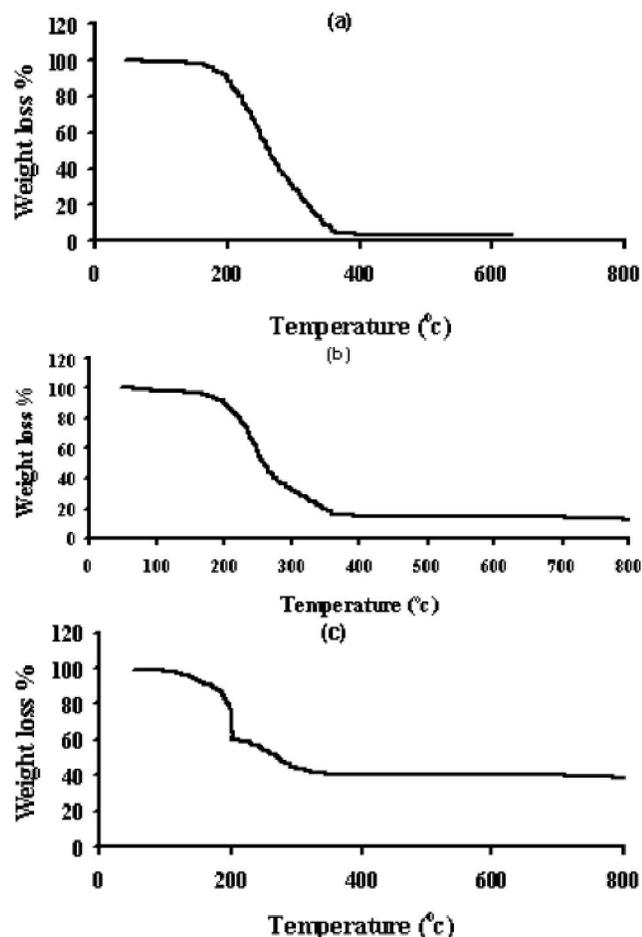
Figure 5 : TGA curves of a) pure PMMA prepared by emulsion polymerization as well as PMMA/Ag nanocomposites prepared by in situ emulsion polymerization in presence of silver nitrate (AgNO₃) with different concentrations, (b) 0.5 wt. %, c) 1.5 wt. %.

UV–visible spectroscopy

The *in situ* emulsion polymerization of MMA monomer was carried out in presence of different concentrations of silver nitrate solutions. The Ag nanoparticles will be formed and will examine using UV-visible spectroscopy, the difference in the metal salt concentration well influence the formation of nanoparticles. Figure 6 shows the effect of varying silver nitrate concentrations on nanoparticles synthesis when the emulsion polymerization was carried out with different concentrations (0.0, 0.5wt %) of silver nitrate, colorless, brown and dark brown colors were observed, respectively. When the silver nitrate concentrations changed from 0.5 wt %, in PMMA nanocomposites the peak of Ag nanoparticles will appear at around 420 nm that prove the formation of Ag

nanoparticles, and this peak became very intensive with increasing the silver nitrate concentration (Figure 6b).
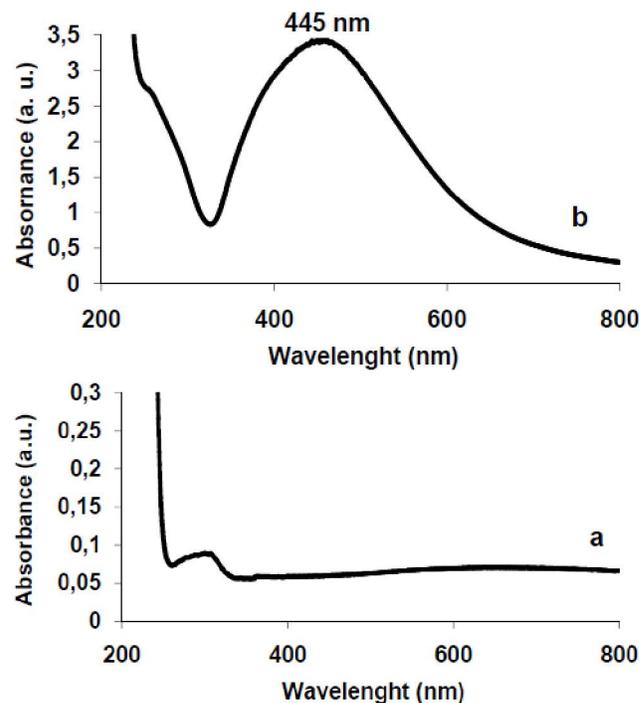
Figure 6 : UV-spectroscopy of pure PMMA (a) as well as PMMA/Ag nanocomposites containing 0.5 wt. % of Ag nanoparticles (b)

CONCLUSIONS

Successfully synthesized AgNPs directly using *in-situ* emulsion polymerization of MMA monomer, PMMA/Ag nanocomposites were characterized using UV spectroscopy and appear characteristic peak at 445 nm related to Ag NPs. XRD, SEM and TEM confirmed the formation of PMMA/Ag nanocomposites containing AgNPs. Thus carbonyl (C=O) of the MMA monomer works effectively for the synthesis of silver nanoparticles. The prepared nanocomposites exhibit more thermal stability more than pure polymer. These in turn, could be applied in the fields of food packaging applications.

REFERENCES

[1] P.Ding, B.Qu; J.Coll.Interf.Sci., **291**, 13 **(2005)**.
[2] S.Vyazovkin, I.Dranca, X.Fan, R; Macromol.Rapid Commun., **25**, 498 **(2004)**.
[3] L.Qiu, B.Qu; J.Colloid Interf.Sci., **31**, 347 **(2006)**.
[4] Y.S.Choi, M.H.Choi, K.H.Wang, S.O.Kim, Y.K.Kim, I.J.Chung; Macromol., **34**, 8978 **(2001)**.

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[5] Z.Matusinoviæ, M.Rogošiæ, J.Šipušiæ; Polymer Degradation and Stability, **94**, 95 **(2009)**.

[6] E.M.Moujahid, J.Inacio, J-P.Besse, F.Leroux; Microporous and Mesoporous Materials, **57**, 37 **(2003)**.

[7] C.Taviot-Gueho, A.Illaik, C.Vuillermoz, S.Commereuc, V.Verney, F.Leroux; J.Phys. Chem.Solids., **68**, 1140 **(2007)**.

[8] C.S.Wagner, Y.Lu, A.Wittemann; Langmuir, **24**, 12126 **(2008)**.

[9] A.Haroun, A.M.Youssef; Synthetic Metals, **161**, 2063 **(2011)**.

[10] A.A.Hebeish, M.M.Abdelhady, A.M.Youssef; Carbohydrate Polymers, **91**, 549 **(2013)**.

[11] M.Nassar, A.M.Youssef; Carbohydrate Polymers, **89**, 269 **(2012)**.

[12] H.S.Zhou, T.Wada, H.Sasabe; Applied Physics Letter, **68**, 1288 **(1996)**.

[13] W.Chen, Y.Yuan, L.Yan; Materials Research Bulletin, **35**, 807 **(2000)**.

[14] A.Vadivel Murugan, C.W.Kwon, G.Campet; Journal of Physic Chemistry B, **108**, 10736 **(2004)**.

[15] V.G.Pol, A.Gedanken, J.Calderon-Moreno; Chemistry of Materials, **15**, 1111 **(2003)**.

[16] R.Vijaya Kumar, O.Palchik, Y.Koltypin; Ultrasonic and Sonochemistry, **9**, 65 **(2002)**.

[17] J.Zhang, Z.Liu, B.Han; Chemistry- A European Journal, **10**, 3531 **(2004)**.

[18] W.L.Chou, D.G.Yu, M.C.Yang; Polymers for Advanced Technologies, **16**, 600 **(2005)**.

[19] J.Zhang, S.Xu, E.Kumacheva; Advanced Materials, **17**, 2336 **(2005)**.

[20] C.H.Collins, P.M.Lyne; Microbiological methods, 5th edition, Butterworth and Co.Ltd., London and Toronto, 167-181 **(1985)**.

[21] G.C.Xu, J.Y.Xiong, X.L.Ji, Y.L.Wang; Journal of Thermoplastic Composites Materials, **20**, 523 **(2007)**.