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Synthesis and Characterization of Ag/PVP Nanocomposites by Reduction Method

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Abstract

A polyvinylpyrrolidone (PVP)/Ag nanocomposite was prepared by reduction of silver nitrate in ethylene-glycol in the presence of a polymeric protective agent (*i.e.*, poly (N-vinylpyrrolidone)). The size dependent color variation of this nanocolloid is a clear indication of the presence of Ag as nanoparticles in the polymer matrix. The nonlinear optical properties were studied by Z-scan technique in which a Q-switched Nd: YAG laser with a pulse width of 7 ns at 532 nm was used as the source of light. Z scan measurement shows that Ag/PVP exhibits third order Nonlinear Optical effects. The peak-valley curve from closed aperture measurement indicates the self-defocusing process. The third order nonlinear optical parameters n_2, β, χ^3 are found to be of the orders of 10^{-9} esu, 10^{-9} m/W, 10^{-11} esu respectively. The very strong Plasmon resonance peak at 419 nm was observed and is a clear consequence of the nanosize of dilute Ag particles. The optical band gap of this nanomaterial was calculated as 2.535 eV. The XRD pattern indicates the presence of crystalline Ag and the average grain size was obtained as 17.4 nm. The SEM micrograph confirms this observation. Thermal Gravimetric Analysis implies that Ag/PVP nanocomposite exhibits high degree of thermal stability.

Keywords

Ag/PVP Nanocomposites, XRD, Optical Band Gap, Z-Scan

Subject Areas: **Applied Physics, Condensed State Physics**

1. Introduction

The polymers embedded with metal nanoparticles are of current research interest because of their novel proper-

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ties generated from quantum size effect of the embedded metal nanoparticles. Polymer metal nanocomposites with varying nano-particle size, shape and concentration are significantly used in many potential optical, electrical and optoelectronic applications [1]. Many synthetic approaches have been applied to the preparation of metal/polymer nanocomposites [2]-[4]. Conventionally, the polymerization of monomers and formation of metal nanoparticles are two processes which occur separately, after which the polymer and nanoparticles are mechanically mixed to form nanocomposites [5]. However, it is extremely difficult to disperse the nanoparticles homogeneously into the polymer matrix, because of agglomeration of nanoparticles and high viscosity of the polymer. In recent years, more attention has been paid to the *in situ* synthesis of metal nanoparticles in polymer matrices. This method is based on the reduction of metal ions that are dispersed in polymer matrix. Many polymer thin films, containing noble metal nanoparticles, have been prepared by reducing polymer metal chelate films such as polyaniline/Au, poly (vinyl alcohol)/Ag, poly (acrylic acid)/Cu [6]-[8]. Among the many polymers, the polyvinylpyrrolidone (PVP) has good film-forming and adhesive behavior on many solid substrates and the films formed exhibit good optical quality (high transmission in visible range), and mechanical strength (easy processing) required for applications.

Keeping in view, the significant importance of doping Ag nanoparticles in polymer films, we have undertaken Ag/PVP composites in order to understand their structural, optical and thermal properties. The primary focus of this study is the measurement of third order nonlinear optical parameters of Ag/PVP nanocomposites.

2. Experimental Procedure

The Ag/PVP nanocomposite was prepared by chemical reduction method [9] as shown in **Figure 1**. The Ag^{+} ions in the $AgNO_3$ (Aldrich) were reduced to Ag atoms by the addition of ethylene glycol (Aldrich). These Ag atoms remain dispersed in the host PVP matrix and the stable Ag/PVP nanocomposite is obtained.

PVP/$AgNO_3$ precipitate obtained from chemical reductionis dissolved in ethylene glycol and is made to a thin film by dip coating technique. Structural analysis of Ag/PVP nanocomposite was carried out using Rigaku Dmax diffractometer equipped with Cu K_α radiations (λ = 1.542 A˚) at 40 KV and 35 mA. The sample in the form of thin film was scanned from 0˚ - 80˚ in steps of 0.020˚ with a step time of 31.2 sec. The surface morphology was studied by using SEM micrographs. It was obtained by using JEOL 6400F SEM at an accelerating voltage of 20 k. The thermal stability of the nanocomposite thin film was determined by Thermal Gravimetric Analysis (TGA). In this, 5.5 mg of the sample was heated from 40˚C to 900˚C at a rate of 10˚C/min and the weight loss with rise in temperature was recorded.

The absorption spectrum of the nanocomposite solution was obtained from a UV-Visible spectrophotometer by scanning the sample under radiation ranging from 200 to1000 nm. The third order nonlinear optical parameters n_2 (nonlinear refractive index), β (nonlinear absorption coefficient) & $\chi^{(3)}$ (third order susceptibility) were calculated by the Z-scan technique. A Q-switched Nd: YAG laser with a pulse width of 7 ns at 532 nm was used as the source of light in the Z-scan experiment. The Z-scan technique was performed by translating the sample along the focus of the sharply focused LASER beam and the power transmitted through the sample was measured. From the open and closed aperture data, the nonlinear absorption and refraction parameters were calculated.

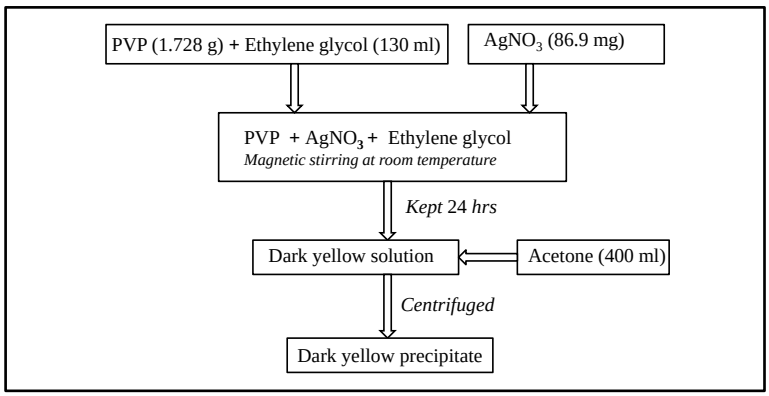


Figure 1. Schematic flow chart for Ag/PVP nanocomposite preparation.

3. Results and Discussion

3.1. Size Dependent Colour Variation

The colour of Ag/PVP nanocomposite solution varies with the percentage of $AgNO_3$ added as shown in **Figure 2**. The PVP in pure form is colourless and when 2% $AgNO_3$ is added, its colour changes to pale yellow. As the $AgNO_3$ concentration in the solution is increased to 5%, the colour changes to dark. This size dependent colour variation is a peculiar effect exhibited by the nanoparticles of noble metals due to the surface plasmon resonance [10]. So, this observation indicates the presence of Ag in the solution as nanoparticles.

The free electrons in the metal (d electrons in silver) are free to travel through the material. The mean free path in silver is 50 nm; therefore when particles are smaller than this, no scattering is expected from the bulk. Thus, all interactions are expected to be with the surface. When the wavelength of light is much larger than the nanoparticle size it can set upstanding resonance conditions. Light in resonance with the surface plasmon oscillation causes the free-electrons in the metal to oscillate. As the wave front of the light passes, the electron density in the particle is polarized to one surface and oscillates in resonance with the light's frequency causing a standing oscillation. The resonance condition is determined from absorption and scattering spectroscopy and is found to depend on the shape, size, and dielectric constants of both the metal and the surrounding material. This is referred to as the surface plasmon resonance.

As the shape or size of the nanoparticle changes, the surface geometry also changes, causing a shift in the electric field density on the surface. This causes a change in the oscillation frequency of the electrons, generating different cross-sections for the optical properties like scattering [11]. 5% $AgNO_3$ solution exhibits pronounced third order nonlinear optical effects and is chosen for further analysis.

3.2. Z-Scan Analysis

Figure 3(a) and **Figure 3(b)** show the typical transmittance curves obtained for Ag nano-fluids prepared by chemical reduction. The open aperture *Z*-scan measurements are taken. The nonlinear absorption coefficient β is calculated by theoretically fitting the experimental data using the equation of normalized transmittance [12]-[14] as,

$$T(z, S=1) = \sum_{m=0}^{\infty} \frac{\left[-q_0\right]^m}{(m+1)^{3/2}}$$

where,

$$q_0(z) = \frac{\beta I_0 \left[1 - e^{-\alpha_0 L}\right]}{\left[1 + \left(\frac{z}{z_0}\right)^2\right] \alpha_0}$$

$Z_0 = kw_0^{\,2}/2$ Rayleigh range; w_0 = the beam waist radius at the focal point.
α_0 = Linear absorption coefficient; I_0 = Peak Irradiance; L = Sample length.

The normalized transmittance open aperture curve for the sample in solution form is given in **Figure 3(a)**. The solid line is the theoretical fit of experimental data, which yields the nonlinear absorption co-efficient β. The curve is symmetric about $z = 0$. The nonlinear absorption is found to be large at the focus point ($z = 0$), where the intensity is high and it results in a minimum transmission.

The closed aperture measurements are taken. From the closed aperture data usually mixed information of nonlinear absorption and refraction is obtained. In order to abstract the information of refraction alone, closed aperture data is divided with that of open aperture and plotted. From pure nonlinear refraction curve, obtained by division of closed aperture scan by open aperture, $\Delta\phi_0$ is calculated by theoretically fitting the experimental data using the equation of normalized transmittance as,

$$T(z) \cong 1 - \frac{4\Delta\phi_0 x}{\left(x^2+9\right)\left(x^2+1\right)}$$

where, $x = z/z_0$

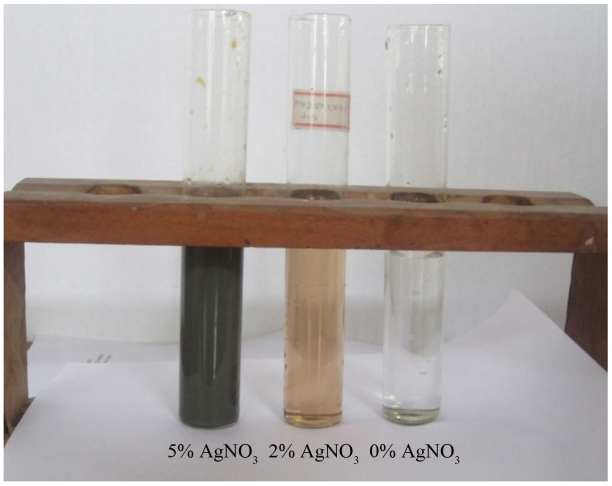
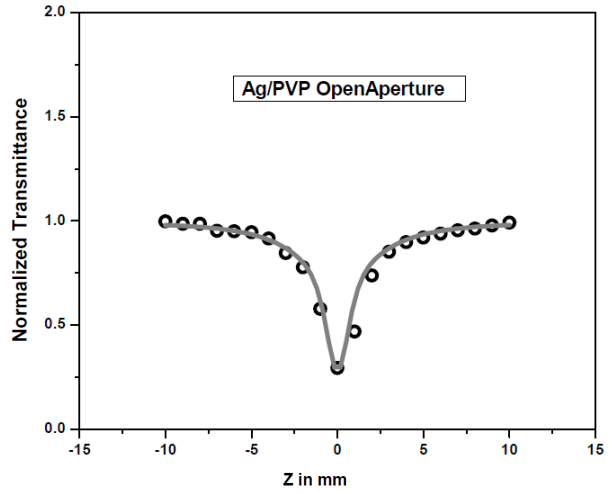
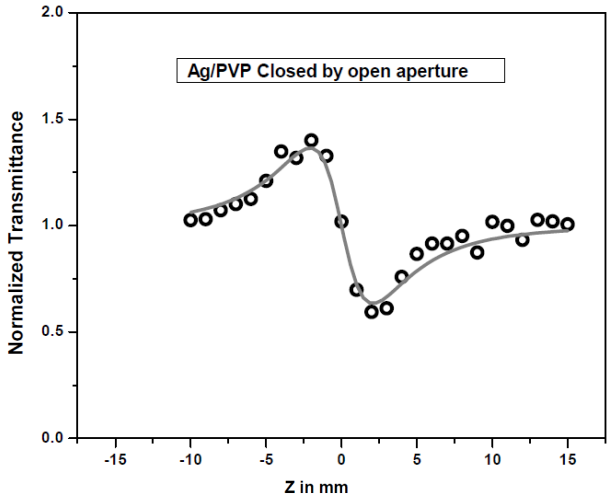


Figure 2. Size dependent colour variation of Ag/PVP nanofluid.



(a)



(b)

Figure 3. (a) Open aperture curve and (b) Pure nonlinear refraction curve.

Nonlinear refractive index is given by,

$$\vartheta\left(m^2/W\right)=\frac{\Delta\phi_0\lambda}{2\pi L_{eff}I_0}$$

$$n_2\left(esu\right)=\frac{cn_0}{40\pi}\vartheta\left(m^2/W\right)$$

$$L_{eff}=\frac{\left(1-e^{-\alpha L}\right)}{\alpha}$$

L_{eff} = Effective thickness; α = Linear absorption coefficient.

The normalized closed/open transmittance curves for the sample are shown in **Figure 3(b)**. This curve is known as the pure nonlinear refraction curve.

The peak-valley configuration of pure nonlinear refraction curve reveals the self-defocusing effect [15] [16] of the sample. That is, the material is having a negative nonlinearity. The calculated values of the 3rd order optical parameter for the sample are tabulated in **Table 1**. The n_2, β and χ^3 values are of the order of 10^{-9} esu, 10^{-9} m/W and 10^{-11} esu respectively.

3.3. Absorption Spectra Analysis

Figure 4 shows the UV-Visible absorption spectra of Ag/PVP nanocomposites. The main peak is observed at λ = 419 nm, that is $h\nu$ = 2.965 eV. For pure PVP the main peak is at $h\nu$ = 4.65 eV [17]. This peak is attributed to the Surface Plasmon Resonance phenomena of free electrons in the conduction band of Ag nanoparticles. Surface Plasmons are coherent electron oscillations that exist at a metal-dielectric interface. The term "Plasmon" refers to the quantum excitation of an electron plasma. Surface Plasmon resonance is the resonant, collective oscillation of conduction electrons in a metal stimulated by incident light. The resonance condition is established when the frequency of light photons matches the natural frequency of surface electrons oscillating against the restoring force of positive nuclei. So, the absorption peak in the visible region—that is, at 419 nm implies that for the free electrons in the conduction band of Ag nanoparticles the resonance occurs when a radiation of wavelength λ = 419 nm incident on it. The peak in the UV region correspond the host PVP polymer.

3.4. Determination of Optical Bandgap

To obtain information about direct inter band transitions; the fundamental absorption edge is analyzed. The absorption coefficient α is related to the photon energy $h\nu$ by:

$$\alpha=\alpha\left(h\nu-Eg\right)^n$$

where, Eg is the optical band gap. The value of nis 1/2 for allowed transitions and 3/2 for forbidden transitions.

The absorption coefficient is given by the relation

$$\alpha=2.303A/t$$

where, A is the absorbance of the film and t is the thickness. Hence the direct allowed band gap is determined by plotting α^2 as a function of photon energy $h\nu$ which gives a straight line as shown in **Figure 5**. The intercept of this straight line on the energy axis (*i.e.*, α^2 = 0) gives the direct band gap. The value of optical band gap obtained from **Figure 5** as 2.535 eV. That is, the value of Eg decreases from 4.90 eV (pure PVP) to 2.535 eV for PVP-Ag nanocomposite. Such a decrease in the value of Eg can be attributed to be due to the formation of bonds between silver nanoparticles and PVP molecules, which form the trap levels between the HOMO and LUMO energy states, making the lower energy transitions feasible and results in the reduction of optical band gap.

Table 1. Nonlinear optical parameters of Ag/PVP nanocomposites.

Sample	n_2 (10^{-9} esu) Nonlinear refractive index	β (10^{-9} m/W) Nonlinear absorption coefficient	$\chi^{(3)}$ (10^{-11} esu) Third order nonlinear susceptibility
Ag/PVP	−2.2	2.28	2.36

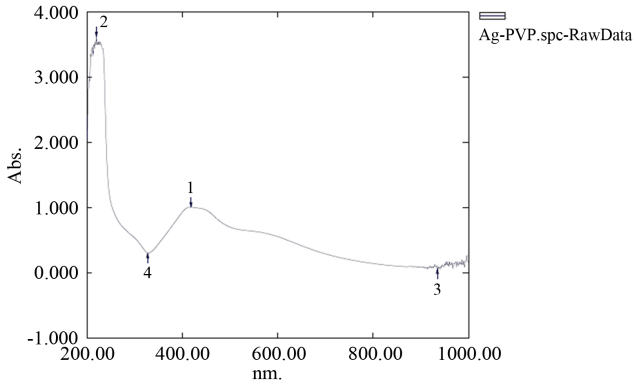


Figure 4. Absorbance versus wavelength spectra of Ag/PVP nanocomplex.

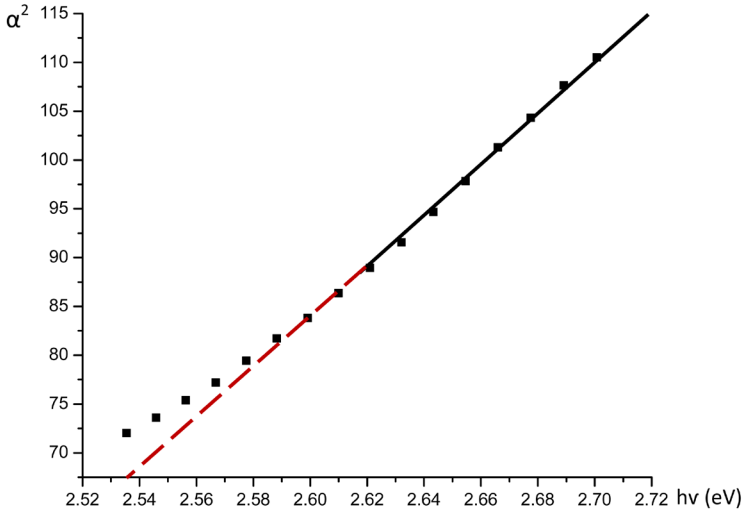


Figure 5. Plot of α^2 versus hν for Ag/PVP sample of thickness.

3.5. X-Ray Diffraction Studies

XRD patterns of Ag/PVP nanocomposite with the 2θ values in the range 0˚ to 80˚ is presented in **Figure 6**. The diffraction peaks at 2θ equal to 38.883˚, 45.070˚, 65.191˚, 78.0860 are in good agreement with the literature values of metallic silver [18] [19]. The average grain size (D) of silver can be determined using Debye Scherrer's relation:

$$D = 0.94\lambda/\beta\cos\theta$$

where λ is the wavelength of the CuK_α radiation, β is the full width at half maximum in radians.

The particle size at 2θ = 38.883˚, where maximum count is observed, is found to be 17.4 nm. So the peaks in the XRD plot imply that Ag^+ ions in the sample are reduced to crystalline silver atoms and are present in the solution as nanoparticles. The broad peak obtained at 2θ equal to 23.288˚ clearly indicates the amorphous nature of the host PVP [20] [21].

3.6. SEM Analysis

The particle size distribution is inspected by Scanning Electron Microscope and the SEM micrographs of the Ag/PVP nanocomplex are shown in **Figure 7**. In **Figure 7(a)** the large sized polymer molecules and big clusters of silver are seen. The part encircled in **Figure 7(a)** is magnified (× 150,000) in **Figure 7(b)**. In the magnified figure we can see that silver particles are distributed and no strong clustering is there. The shape of the Ag nanoparticles varies from spherical to pseudo spherical. The function of PVP in the Ag/PVP composites is not only

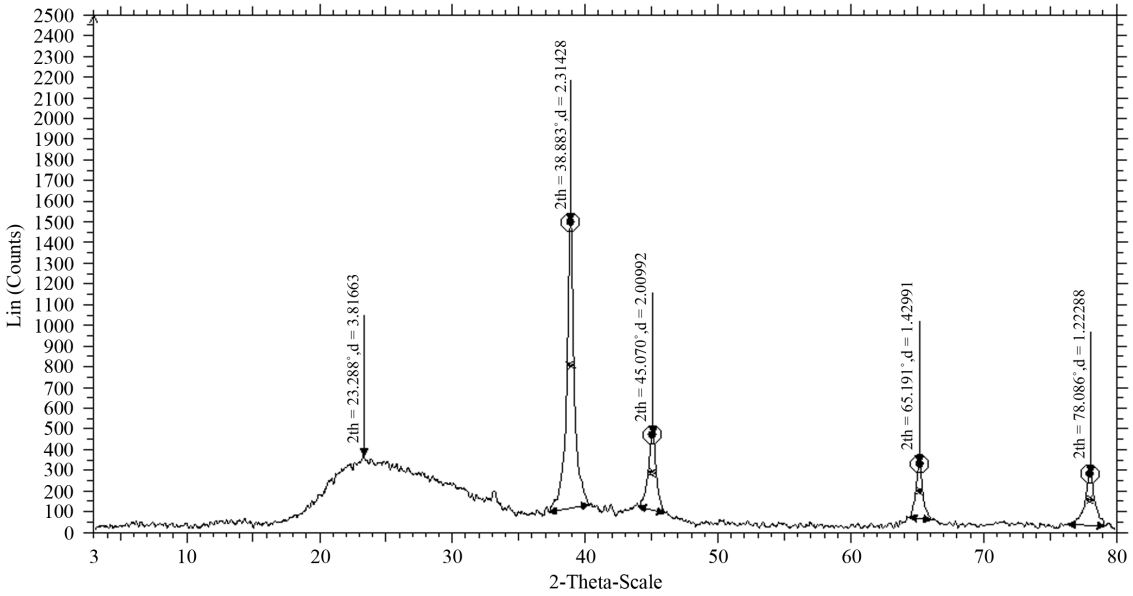
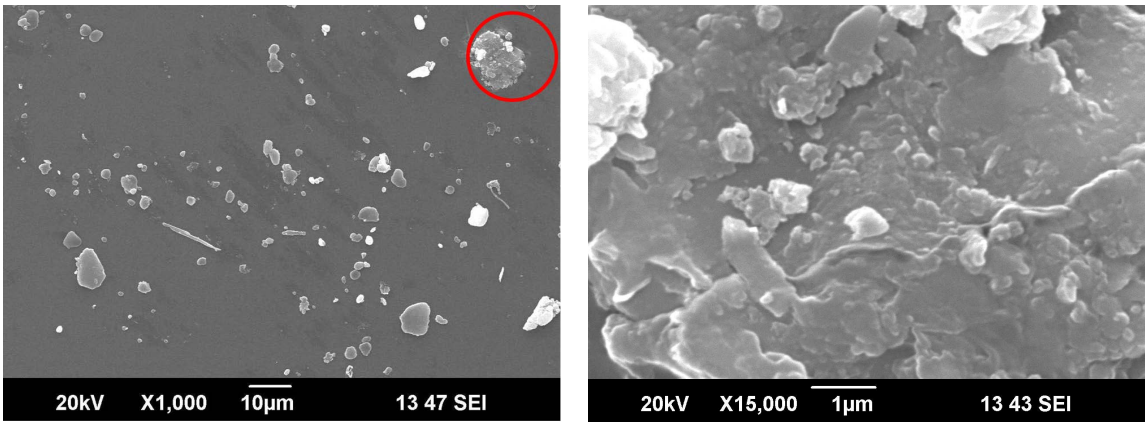


Figure 6. XRD pattern of Ag/PVP polymer film.



(a) (b)

Figure 7. (a) SEM image of silver nanoparticles dispersed in PVP (solution in ethylene glycol); Scale bar (10 µm). (b) Magnified version; Scale bar (1 µm).

as a binder, but it also prevents the process of agglomeration of Ag nanoparticles [22]-[24] and limits the diameter of the nanoparticles formed.

The diameter of a silver atom is 0.3 nm. Consider a silver nanoparticle of diameter 17 nm present in the polymer matrix. This nanoparticle contains about 181,962 atoms of silver, which is a small in comparison with the Avogadro number (10^{23}). Such a low number allows any atom in that cluster to scatter light. The resulting behavior of the nanocomplex will be different from that of the bulk material.

3.7. Thermal Gravimetric Analysis

The Thermal Gravimetric Analysis (TGA) was carried out on Ag/PVP nanocomposites and the result is compared with the TGA profile of pure PVP. **Figure 8(a)** & **Figure 8(b)** show the TGA profile for pure PVP and Ag/PVP complex respectively. For Ag/PVP complex (**Figure 8(b)**), the initial weight loss was calculated to be around 2% when heated up to 250˚C. The weight loss may be due to the volatile impurities present in the sample. The second major weight loss above 350˚C indicates the structural decomposition of Ag/PVP nanocomposites. This decomposition profile starts from 350˚C and continues up to around 450˚C. From the literature data for

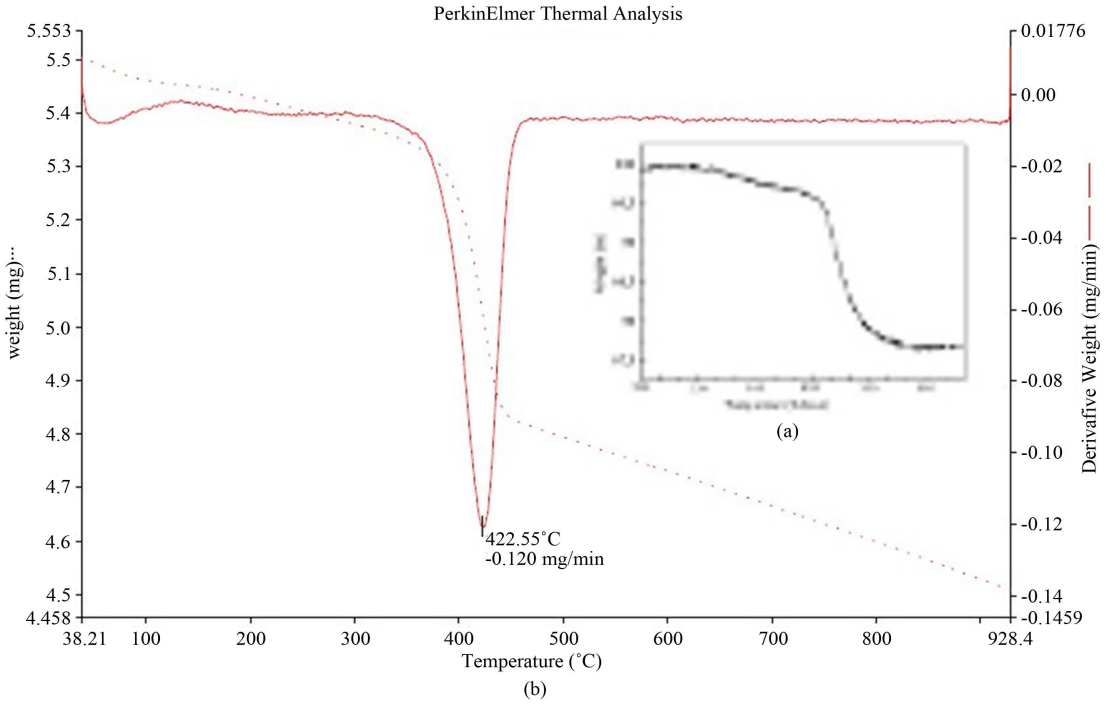


Figure 8. (a) Thermogram of Pure PVP. (b) TGA thermogram of Ag/PVP film.

pure PVP polymer [25] it is found that the structural degradation takes place at about 300˚C and complete decomposition occurs at 500˚C. This shows that the thermal stability of the polymer is improved due to the presence of Ag nanoparticles.

4. Conclusion

Chemical reduction method for the preparation of Ag/PVP nanocomposites offers advantages of atomic level control and uniform distribution of nanoparticles. Here the size dependent colour variation of Ag/PVP composite is a clear indication of metallic Ag present as nanoparticles. X-ray diffraction studies and SEM images also confirm this observation. Ag/PVP nanocomposite is found to resist the thermal degradation up to a high temperature. Optical absorption spectra exhibit interesting features which are the characteristics of Ag nanoparticles. The presence of absorption peak at 419 nm is a clear signature of Surface Plasmon Resonance occurring in Ag nanoparticles. Optical bandgap of this nanocomplex is obtained as 2.535 eV. Third order nonlinear optical effects exhibited by 5% $AgNO_3$ solution are studied by Z-scan technique. Nonlinear absorption coefficient β, nonlinear refractive index n_2, and third order susceptibility $\chi^{(3)}$ are found to be of the orders of 10^{-9} m/W, 10^{-9} esu and 10^{-11} esu respectively. The peak-valley curve in closed aperture data indicates the self-defocusing effect displayed by this solution. The reduced dimension of metallic silver accounts for the peculiar properties of Ag/PVP nanocomplex and is a promising material for optical applications.

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