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Synthesis and ultrasonic characterization of nanofluid containing silver nanoparticles

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ABSTRACT

A polymer colloidal solution having dispersed nanoparticles of Ag metal has been developed using a novel chemical method. Colloidal solutions of representative concentrations of 0.2 to 5.0 wt% Ag-nanoparticles contents in the primary solutions were prepared to study the modified ultrasonic attenuation and ultrasonic velocity in polyvinyl pyrrolidone (PVP) polymer molecules on incorporating the Ag-nanoparticles. The synthesized silver nanoparticles dispersed in the polymer solutions were characterized by UV-Visible absorption spectroscopy, X-ray diffraction (XRD) and Transmission electron microscopy (TEM). The nanofluid sample showed a symmetrical peak at 410 nm due to the surface plasmon resonance of the silver nanoparticles. XRD results confirmed that silver nanoparticles were crystalline in the colloidal solution. The TEM micrograph revealed spherical silver nanoparticles having diameter in the range 10-30 nm. A characteristic behaviour of the ultrasonic velocity and the attenuation are observed at the particular temperature / particle concentration. It reveals that the colloidal suspension occurs in divided groups in the small micelles. The results are discussed in correlation with the thermophysical properties predicting the enhanced thermal conductivity of the samples.

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KEYWORDS

Nanofluids;
Colloids;
Silver nanoparticles;
Ultrasonic properties;
UV-visible;
TEM.

INTRODUCTION

Nanomaterials have unique mechanical, optical, electrical, magnetic and thermal properties. Nanofluids (nanoparticles-fluid suspensions) are engineered by suspending nanoparticles in traditional heat transfer fluids such as water, oil, ethylene glycol etc. A very small amount of guest nanoparticles, when dispersed uniformly and suspended stably in host fluids, can provide dramatic improvements in the thermal properties of host

fluids. More recently there has been an increasing interest in the acoustical properties of suspensions for acoustic telemetry through drilling fluids as well as arising demand for ultrasonic particle size instrumentation. Commercial instrument have been developed to characterize the properties of suspensions using ultrasound^[1]. Several scientists have made the study of ultrasonic propagation behaviour through the suspension of solid particles particularly in micrometer or millimeter size in a liquid aiming to identify the mechanism that enable

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useful information to be extracted from the behaviour of ultrasonic properties, such as particle size, concentration and mechanical properties of the constituents [2-5]. Polymers have been found effective stabilizers of colloidal metal nanoparticles. In particular, polyvinyl pyrrolidone (PVP) is used in recent synthesis of various silver nanoparticles. Recently, polymer nanofluids are the subject of considerable interest because of the unique properties that can be achieved with these materials. At the same time, because of their high surface to bulk ratio, nanoparticles suspended polymer matrix significantly are revealing some new properties which are not present in either of the pure materials. Therefore, the investigation of the influence of nanoparticles on the properties of a polymer matrix is necessary in order to be able to better predict the final properties of the complex fluids. In the present work we have made the study of the ultrasonic attenuation and velocity in a polymer colloidal solution with dispersed Ag-metal nanoparticles (nanofluid). The colloid solutions used here have been developed by in-situ dispersion and reduction of Ag^+ cations to Ag-metal of divided nanoparticles in polymer molecules of refreshed reactive nascent surfaces of PVP in an aqueous solution at an elevated temperature. The results are analyzed and discussed in correlation with the microstructure and improved thermal properties of the complex nanofluid.

EXPERIMENTAL

Synthesis of polymeric nanofluids

A freshly prepared homogeneous colourless transparent PVP aqueous solution has been used. It was obtained by dissolving 3.0g PVP in 100 ml of double distilled water. A continuous stirring over a magnetic stirrer at a constant temperature of 50-70°C promotes the PVP dissolution in water in a clear solution. An aqueous solution of AgNO_3 (1.0 M concentration) has been used to derive an Ag-PVP colloidal nanofluid. Adding AgNO_3 solution to the PVP solution while stirring the total solution carries the proposed reaction. In this way, Ag-PVP solutions of selected Ag contents of 0.2, 0.5, 1.0, 2.0 and 5.0 wt% in 100ml total solutions were prepared. They were used as stock solutions to perform the proposed ultrasonic velocity and ultrasonic

attenuation studies in Ag-PVP colloids.

Spectroscopy and microscopy measurements

The absorption spectrum was recorded using a Lambda 35, Perkin-Elmer double beam UV-visible absorption spectrometer. A film of the nanofluid was dried on the glass plate for X-ray diffraction analysis. XRD measurement was done by X'Pert-Pro, PANalytical (with $\text{CuK}\alpha$ radiation $\lambda=1.5406 \text{ \AA}$) operating at room temperature. The particle size and its distribution were analysed with E.M.-C.M.-12 (Philips) transmission electron microscope operating at 200 KeV. The samples for TEM measurements were prepared by dropping the colloidal solution onto a copper grid.

Ultrasonic velocity and ultrasonic attenuation measurements

Ultrasonic velocity measurements have been made at 2MHz of frequency with help of a variable path interferometer. Water is circulated around the sample using a specific thermostat. The measured value of ultrasonic velocity is accurate to $\pm 0.1\%$ with an error of measurement of 0.5°C in temperature. The ultrasonic attenuation (α/l^2) measurements have been made by a pulse-echo technique. The measured value of (α/l^2) is accurate to $\pm 5\%$. The standard liquids have been used to check the calibration and accuracy of the measurements. Pulses are sent by a 15 MHz quartz crystal and the decay is observed on the cathode ray oscillograph. The decay is made exponential by adjusting the leveling screws and adjusting the crystal and the reflector parallel to each other. The measured value of the temperature is accurate to $\pm 0.5^\circ\text{C}$ as in the ultrasonic velocity measurements.

RESULTS AND DISCUSSION

Physical properties of polymeric colloids

When adding an AgNO_3 solution (1.0 M) to a PVP solution (3.0g/100ml) in water, a polymer complex forms by a redox reaction of AgNO_3 with the PVP molecules of refreshed reactive nascent surfaces caused during the processing using the mechanochemical stirring under heating conditions of the solution. The reaction occurs in steps, depending on the initial concentrations in



Figure 1: Photograph of the colour of the samples: [1] Pure PVPm, [2] 0.2 wt% Ag-PVP, [3] 0.5 wt% Ag-PVP, [4] 1.0 wt% Ag-PVP, [5] 2.0 wt% Ag-PVP, [6] 5.0 wt% Ag-PVP

the two solutions and other experimental conditions. Ultimately, a colloidal solution consisting of Ag metal nanoparticles embedded in a moiety of modified PVP molecules appears in a colloid complex in a characteristic equilibrium colour. The occurrence of a stable coloured polymer complex in this reaction is indicative of formation of an inorganic-organic colloid of a stable microstructure. The photographs of the colour of the samples are shown in figure 1.

Following our experimental observation, it is proposed that the reaction process involves a cross-linking of PVP in a specific polymer structure of an enhanced viscosity of the average value in the two reaction components of (i) AgNO_3 solution and (ii) the PVP polymer solution. Figure 2 shows the UV-visible spectrum of the silver nanoparticles-polymer suspension. The UV-visible spectrum shows a strong absorption peak at 410 nm due to the plasmon oscillation modes of conduction electrons in the colloidal nanoparticles-liquid suspensions. The crystal structure of the Ag-nanoparticles dispersed in this polymer complex is examined with X-Ray diffraction. Figure 3 shows the XRD pattern of the nanofluid. All the peaks on the XRD pattern can be indexed to that of pure silver metal (JCPDS, File no.04-0783). The peaks are corresponding to the 111, 200, 220 and 311 planes respectively. The average crystalline size of the silver nanoparticles was calculated to be 11 nm according to the half width of the 111 diffraction peak using the Debye-Scherrer formula. The Ag-nanoparticles occur in the usual cubic crystal structure (F_{m3m} space group).

Figure 4 shows the TEM images of the silver nanoparticles-polymer suspensions with corresponding particles size distribution. The TEM images reveal

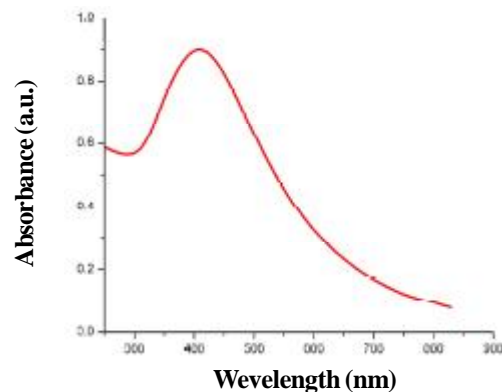


Figure 2: UV-visible absorption spectra of the synthesized silver nanoparticles-polymer suspensions

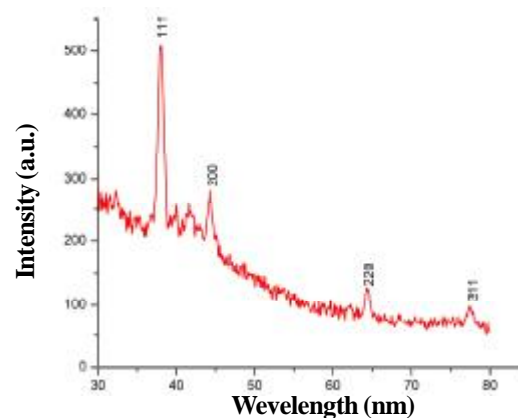


Figure 3: XRD pattern of the silver nanoparticles dispersed in PVP

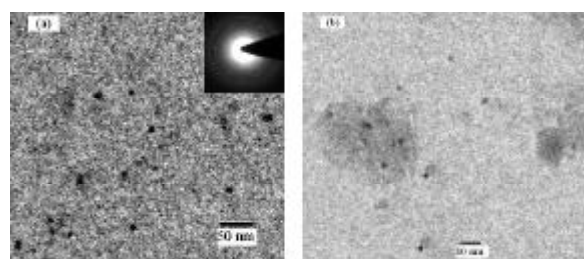


Figure 4: TEM images of the silver nanoparticles-polymer colloidal solution (a and b). Inset shows the electron diffraction pattern revealing the crystalline structure of the Ag nanoparticles

that the silver nanoparticles are spherical in shape with sizes around 10 nm and clusters with size distribution between 10-30 nm. The silver particles are well dispersed in colloidal solution as evidenced by TEM micrographs. The corresponding selected area electron diffraction pattern is displayed in the inset of figure 4(a). It can be indexed to the reflection of face-centered cubic structure verifying the results obtained by XRD pat-

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tem.

Ultrasonic velocity and ultrasonic attenuation

As the ultrasonic velocity is highly sensitive to the local structure, we applied it here to examine its value in Ag-PVP polymer colloids at selected temperatures in the 5-70°C range. All the measurements are made at the frequency of 2 MHz. The results of the temperature dependent ultrasonic velocity and ultrasonic attenuation are presented in figures 5 and 7 respectively.

The result of concentration dependence of ultrasonic velocity is shown in figure 6. The results are showing the effect of Ag nanoparticles on the ultrasonic velocity and attenuation. Figure 5 shows that the ultrasonic velocity in the Ag+PVP polymer colloids increases with temperature. A perusal of figure 5 reveals that there are velocity maxima at 60°C in case of 1.0, 2.0 and 5.0 wt %, Ag-np in PVP colloidal solution. There is a minimum at 30°C in case of 1.0 wt% Ag-np in PVP sample. For the case of 0.2 wt % and 0.5 wt% Ag-nanoparticles in PVP, the velocity increases up to 40°C and after then it remains constant. Figure 6 shows that there is a velocity maximum at 0.5 wt% concentration. Figure 7 demonstrates that the attenuation decreases with temperature and maximum value of attenuation (α/f^2) is found at 20 °C in 5.0 wt% Ag+PVP polymer colloid sample. A perusal of ultrasonic velocity and attenuation plots reveals that the temperature dependency of the ultrasonic velocity and the ultrasonic attenuation does not follow a linear curve. This seems to be in contrary to the results in a sample of pure Ag metal. In general, as in other materials^[6], both the ultrasonic velocity and the ultrasonic attenuation are quite sensitive to the particles size, morphology and dispersion of the particles. A macroscopic interaction of Ag particles with the PVP molecules appears to be a critical parameter to control their final values in this specific example of an inorganic-organic polymer nanocolloidal solution. The effective attenuation in this example can be expressed as:

$$\alpha = \alpha_p + \alpha_m + \alpha_{pm} \quad (1)$$

where α_p is the contribution from the Ag-metal, α_m is the counterpart contribution from the polymer matrix, α_{pm} describes the change in the final α -value owing to a macroscopic interaction between the two components in an Ag-PVP nanocolloid structure and associated modified thermophysical properties of the nanofluid.

S.Biwa et al.^[2] analysed the ultrasonic attenuation

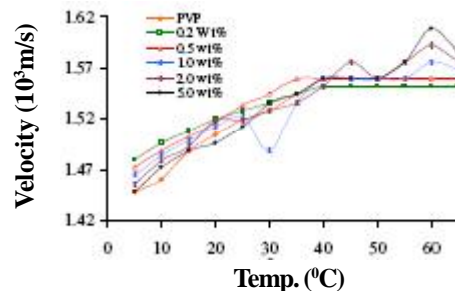


Figure 5: Ultrasonic velocity in Ag+PVP samples vs temperature

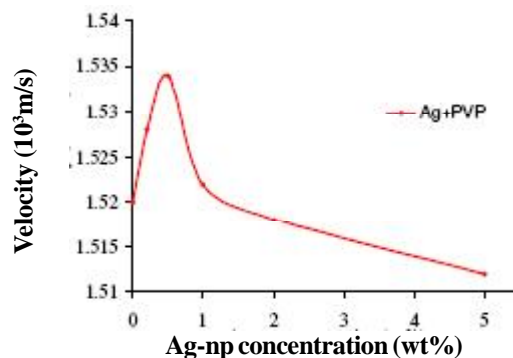


Figure 6: Ultrasonic velocity in Ag+PVP samples vs concentration

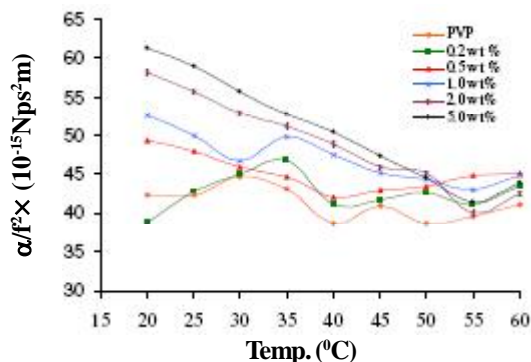


Figure 7: Ultrasonic attenuation in Ag+PVP samples vs temperature

in millimeter sized particles-reinforced polymers by a differential SCHEME and found good agreement between the theory and experiments. The wave attenuation in these composites is a complex process where the viscoelastic loss and the scattering loss coexist. It is also important to recognize that the relative contributions of these loss mechanisms may change not only depending on the acoustic properties of the constituent (matrix and particles) but also according to the particle size, particle concentration and the frequency of inter-

est. In the differential scheme, the changes of macroscopic properties of the complex due to infinitesimal increase of particles concentration are given in differential (incremental) forms. Thus the composite with the particle volume fraction is regarded as a homogeneous effective medium with the equivalent macroscopic properties given by the Lamé moduli λ and μ as well as the density (ρ). The complex moduli λ and μ of an isotropic viscoelastic medium can be given in terms of the ultrasonic velocities and ultrasonic attenuation coefficients of longitudinal and shear waves. The complete description of this theoretical model which we have tried to apply is given in the reference^[2]. The significant attenuation due to scattering by the particles-reinforced was incorporated in the total attenuation in their theoretical model^[2]. The observed attenuation in our case could not be explained by the exact theoretical model following the differential scheme. We found that the attenuation due to scattering from the Ag-nanoparticles in the nanofluid is not significant. It is also important to note that the characteristic behaviour of the ultrasonic attenuation in the Ag+PVP nano-colloids is not found in any of the individual components of the composite^[7-8]. Calculated value of the ultrasonic attenuation in the sample (0.2wt% of the nano-Ag particles) for 15 MHz at 300K following the differential scheme including the ultrasonic absorption due to nanoparticles and thermoelastic loss following the Mason scheme comes 95.83×10^{-3} Np/cm. Here the thermal conductivity 'K' of the nanoparticles for the calculation of thermo-elastic loss has been taken following the molecular dynamics method. Here we incorporated the attenuation due to thermoelastic loss determined by the formula $\alpha_{th} = \omega^2 \langle \gamma_i^j \rangle^2 KT / (2\rho V_L^5)$. Here K is thermal conductivity, $\omega(2\pi f)$ is frequency of the ultrasonic wave, γ_i^j is Gruneisen number, T is the temperature in Kelvin scale, ρ is the density, V_L is the ultrasonic wave velocity. Here we have not incorporated the thermal conductivity of complex thermoelastic medium of our nanofluid as it is not known to us. As the above formulations attenuation due to thermoelastic mechanism is directly proportional to the thermal conductivity of the samples. The total observed attenuation in our experiment for the sample is 107.8×10^{-3} Np/cm. At this juncture it is interesting to investigate the source of excess ultrasonic attenuation.

Most importantly scientists have been perplexed

by the thermal phenomena behind the recently discovered nanofluids like the present samples. One fascinating feature of nanofluids like copper-ethylene glycol is that they have anomalously high thermal conductivities at very low nanoparticles concentrations^[9-11]. To date, the exact mechanism of thermal transport in nanofluids is not fully known, and several possible mechanisms based on theoretical models, experiments and previous heat transfer theory have been suggested to describe experimental results on thermal conductivity of nanofluids. Brownian motion of suspended nanoparticles is attributed as one of the key factors of the greatly enhanced thermal conductivity performance and it was not considered in conventional thermal transport theory. Recently Prof. J.Philip has confirmed the anomalous enhancement in the thermal conductivity of the nanofluids of Au nanoparticles in PVP suspensions by photoacoustic measurements (The work was presented in the National Symposium on Ultrasonics, India in 2007). This enhancement is seen characteristic in nature at particular temperature and particle concentration of the Au nanoparticles-suspensions. The Brownian motion of nanoparticles at the molecular and nanoscale level is considered as a key mechanism governing the thermal behaviour of nanoparticles-fluid suspensions (nanofluids). U.S.Choi et.al. proposed the theoretical model that accounts for the fundamental role of dynamic nano particles in the nanofluids^[10]. They have derived a general expression for the thermal conductivity of nanofluids involving different modes of energy transport in the nanofluids. The important mode is thermal interaction of dynamic or dancing nanoparticles with base fluid molecules. Even though the random motion of nanoparticles is zero when time averaged, the vigorous and relentless interactions between liquid molecules and nanoparticles at the molecular and nanoscale level translate into conductions at the macroscopic level, because there is no bulk flow.

Although the FTIR spectra of Ag-PVP is not available but in the FTIR results of Ag-nano+PVA, disappearance of several bands (837, 711, 650 and 570 cm^{-1}) on increase in the Ag-nano filler content in Ag + PVA suggests that the interaction between Ag-nano particles and the matrix molecules takes place^[12-14]. Also, X-ray photoelectron spectrum (XPS) spectra of Ag+PVP nanocomposite reveal the interaction between

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Ag-nano particles and the matrix PVP^[15].

Thus we may postulate that the Brownian motion of the Ag-nanoparticles in nanofluids produces convection like effects at the nanoscale. Moreover, the thermal conductivity model not only captures the concentration and temperature dependent conductivity, but also predict strongly size-dependent conductivity. As we know, thermo-elastic ultrasonic attenuation is directly proportional to the thermal conductivity of the composite and the attenuation due to scattering for the nanoparticles is negligible. Therefore, we may predict that the effective increased thermal conductivity of this nanofluid has such an impressive effect as the excess attenuation on the total ultrasonic attenuation behaviour. Thus, we have developed ultrasonic mechanism to predict enhanced thermal conductivity due to suspension of the metallic nanoparticles with very low concentration into polymeric fluid.

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