Structural and Thermal Behavior Evaluation of Ag-PVA Nanocomposites Synthesized via Chemical Reduction Technique

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ABSTRACT

Silver nanoparticles were prepared via process of chemical reduction using sodium borohydride as reductant. The prepared nanoparticles were then utilized for synthesizing various compositions of nanocomposites with polymeric matrix of poly (vinyl alcohol). For doing so, the nanoparticles were dispersed in the polymer solution by vigorous stirring. The solutions of the nanocomposites were cast in films. The nanocomposite films were used for various characterization techniques; out of which three are being reported in this communication; XRD, TGA/DTA and SEM. The upshot of XRD proposes a semi-crystalline nature of synthesized nanocomposite. The crystalline character of the nanocomposite enhances with an increasing doping concentration of the prepared nanoparticles. Thermal analysis suggests the degradation pattern of the polymer nanocomposite material and represents that thermal stability improves as the silver nanoparticles are added. The SEM micrograph reveals a uniform surface with a well dispersed nanoparticle in the polymer matrix.

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1. Introduction

Nanocomposite materials have gathered attention of the research community over the past few years. The nanocomposites offer a variety of applications in various fields of technology (Ismail, Salleh, & Ahmad, 2011) and daily life e.g. charge storing devices, conducting materials, (Liu, Xue, Zhang, & Zhai, 2014) magnetic (Azhar Khan et al., 2015) devices, biology(Uppugalla, Male, & Srinivasan, 2014), superconductors (LeBaron, Wang, & Pinnavaia, 1999) and super capacitors (Burke, 2000) etc. The emergence of interest towards the conducting polymers and their interactions with inorganic nanoparticles has opened new horizons of research and technology to make a variety of conducting nanocomposites. These materials can be used to obtain maximum performance in their target devices(Radja, Djelad, Morallon, & Benyoucef, 2015).

Out of many reported methods of preparation of nanocomposites using the filler material and polymer matrix, three of the main methods comprise solution-intercalation, melt-compounding and in-situ polymerization. In this regard photopolymerization has been used extensively in order to prepare nanocomposites from the monomers and the filler material (Decker, Keller, Zahouily, & Benfarhi, 2005). In order to prepare a nanocomposite material it is very pertinent that the components of the nanocomposite should be compatibilized (Larraza, Peinado, Abrusci, Catalina, & Corrales, 2011) so as to get the

maximum of the synergic effect of both the components of the resulting material (Nasar, Khan, & Khalil, 2010). The properties of the nanocomposite actually depict the degree of compatibility of matrix and the filler material involved in the manufacture of nanocomposite. XRD has been one of the most prominent tools employed for investigating assembly structure of composite material. In the current study we have tried to find a relation between the concentration of nanoparticles with the structure and thermal properties of the nanocomposite.

2.   Experimental Procedure
2.1.   Chemicals Used

In this study, the following substances were employed. Silver nitrate, Poly (vinyl alcohol) (PVA Approximately 125,000 g / mol), Poly vinyl (pyrrolidone), Sodium borohydride, De-ionized water as solvent.

2.2.   Synthesis of PVA/Ag Polymer Nanocomposites

Before using, the PVA and other ingredients were vacuum dried. De-ionized water was used to make a stock solution of PVA (5 percent w/w). In 100-gram milipore grade water, 0.45 gram of sodium borohydride was added and dissolved. In the same way, silver nitrate solution was prepared by dissolving 0.75-gram silver nitrate in 250 gram de-ionized water. An ice bath was used to chill a freshly made sodium borohydride solution. With constant vigorous stirring, solution of silver nitrate was added to solution of borohydride slowly by dripping via burrete.

When a rich yellow tint appeared, the procedure was halted. Poly (vinyl pyrrollodone) solution (2 percent) was added to the reaction mixture at this point in order to stabilize the freshly prepared nanoparticles. In an airtight flask, the solution was kept. Five fractions containing various percentages of silver nanoparticles were introduced to different beakers containing five solutions of PVA from the mother solution. For 12 hours, each solution was magnetically stirred.

2.3.   Casting

In Petri dishes (diameter = 14 cm), five different solutions of different concentrations of prepared nanocomposites were put. For film formation, a series of petri dishes arranged on a flat platform at ambient temperature. The solvent evaporation technique produced smooth and homogeneous films. Dried and finished films were carefully removed from petri dishes and were sized into suitable designs and dimensions for various characterization procedures.

2.4.   Characterization

To characterize the produced polymer composites, the following characterization procedures were used.

2.4.1.XRD Analysis

The produced nanocomposite samples were characterized for X-ray diffraction using the "Rigaku (Japan) FX Gieger Series RAD-B system." For this, a one-square-inch sample size was used. The cut sample was then fixed into a sample holding assembly with a 35 kV acceleration voltage. Scanning angles ranged from 10 to 50 degrees, with a current of 20 mA used for X-ray diffraction.

2.4.2.Thermal Analysis

The thermal behaviour of the produced nanocomposite material was evaluated using "Diamond TG/DTA machine manufactured by Perkin Elmer Instruments, USA". The machine's sample chamber was filled with 5-8 mg. The heating rate was kept uniformly at 5°C/ min using an automated furnace. For a few minutes, the temperature was kept 30°C while being exposed to air pressure and gases before releasing Nitrogen gas to the sample

room in a constant state. All other variables were kept constant while heating was initiated. From 30°C to 600°C, the heating was maintained at a constant rate. The mass loss was calculated as a function of temperature using various samples, thus TG/DTA graphs were attained.

2.4.3. Scanning Electron Microscopy

Morphological studies were carried out for silver-PVA nanocomposite samples using a "JEOL Microscope SEM SJ-6490LVMA made in Germany." The result of the same study made a sense of how nanoparticles contained in the polymer matrix were distributed. The nanocomposite images were collected at voltages ranging from 5 kilo Volt to 20 kilo Volt. Image resolutions ranging from 500 X to 100,000 X were employed.

3.   Results and Discussion
3.1.   X-Ray Analysis of PVA /Ag Composite

Results of XRD pattern of the prepared nanocomposites are shown in Figure 1. Mass of the nanoparticles in the said samples ranged from 1 mg to 5 mg, containing a middle value of 3 mg. The sample's crystalline behaviour is depicted in the figure. The outcome is consistent with previous research (Park et al., 2006). The nanocomposite samples exhibit a larger region from $2\theta=5°$ to 11°, followed by a peak at 19.3°, 29.3°, followed by relatively lesser intensity peaks at 26.3°, 35.89°, 39.1°, 42.87°, 47.3°, and 48.3°. The findings support the hypothesis that adding silver nanoparticles improves the crystalline character of resultant material as compared to pure polymer. The peak intensity at $2\theta =19.3o$ attributable to PVA tends to diminish as a function of greater amount of Ag nanoparticles, resulting in higher intensity of neighboring peaks. Similar findings have been reported in previous investigations (Kaczmarek & Podgórski, 2007).
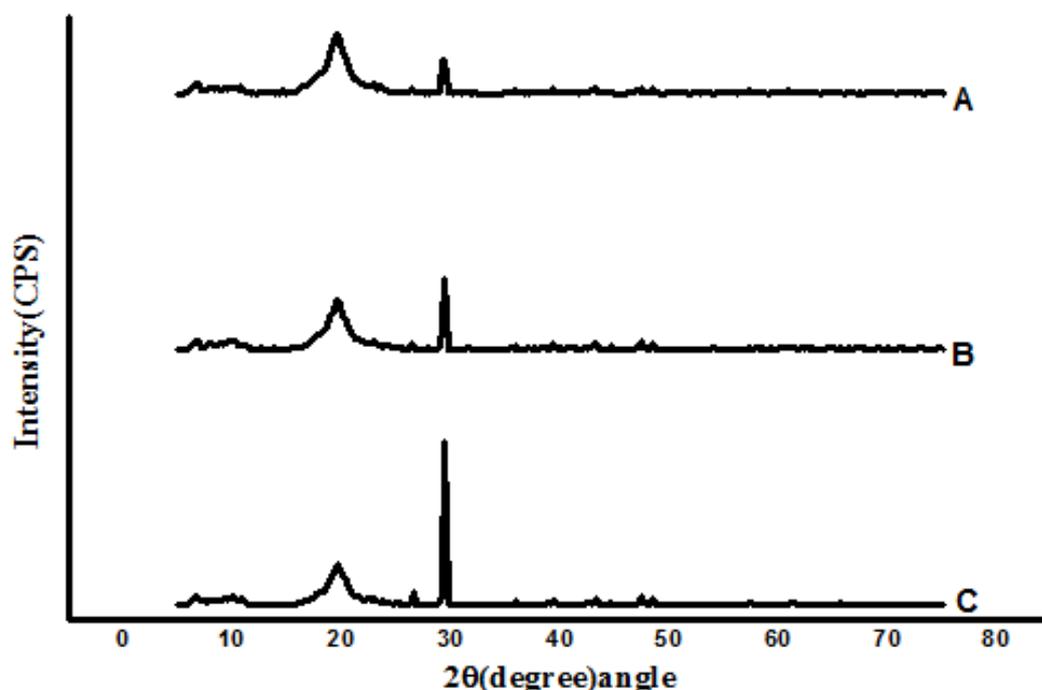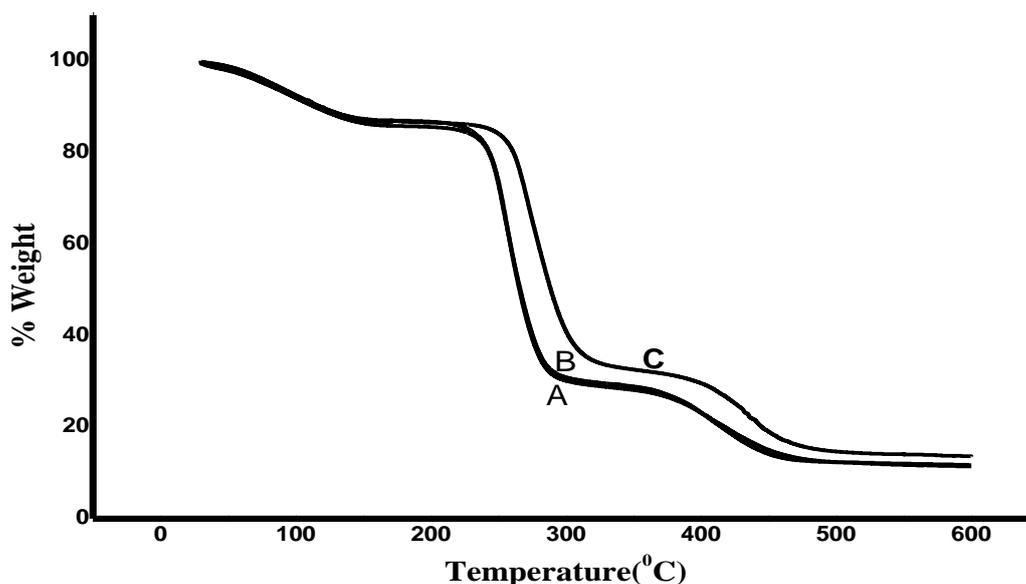

Figure 1: XRD results of Ag-PVA nanocomposites of A: 1mg Ag NP, B: 3mg Ag NP and C: 5mg Ag NP

As evidenced by the other strong peak, a peak with lesser intensity suggests greater amorphous character. Overall, as evidenced by the peaks in the picture, the introduction of silver nanoparticles improves crystalline character of prepared nanocomposite material.

3.2. Thermal Analysis of PVA /Ag Composite

Differential thermal gravimetric analysis and thermo gravimetric testing were performed on selected samples of the produced nanocomposites. The outcomes are shown in Figure 2. The nanocomposite lost weight in three stages, according to the researchers. For three different samples, thermal degradation occurred at 417K, 428K, and 430K respectively. The first step entails each sample losing 12.5 percent, 14 percent, and 13 percent of its weight, respectively. Evaporated water is responsible for this portion of the weight loss, resulting in a completely dried sample. Chemical degradation occurs at 473K. For all three samples, this procedure resulted in a decrease in mass at the rate of 56.5, 55, and 52 % respectively. The next phase is combustion, which occurs after the introduction of oxygen gas in the sample chamber at 573 degrees Fahrenheit. After this phase, increasing the temperature shows no discernible effect. Figure 3 reveals thermal investigations showing that thermal stability is a function of doping of filler in the prepared material.

Figure 2: TGA of Ag-PVA nanocomposites of A: 1mg Ag NP, B: 3mg Ag NP and C: 5mg Ag NP
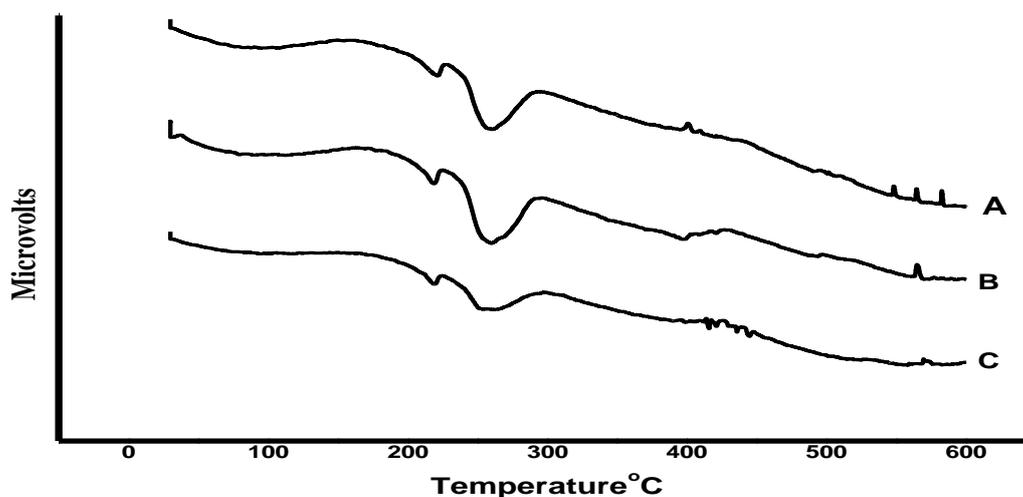
Figure 3: DTA of Ag-PVA nanocomposites of A: 1mg Ag NP, B: 3mg Ag NP and C: 5mg Ag NP

3.3. Scanning Electron Microscopy

The results of morphological study of the surface structure of silver nanoparticlesare shown in Figure 4. This micrograph was magnified by a factor of 100,000. The size of the particles is indicated by markers, as seen in Figure 4. The size of silver nanoparticles spans from 15nm to 40nm, as can be shown. Similarly the results of the morphological study of the nanocomposite material is shown in Figure 5. The sample thickness was between 100 and 200 m. The micrograph shows a smooth morphology of the sample film attributed to the greater degree of compatibility of the filler and the matrix, which results in a homogenous structure of the prepared material having evenly distributed filler particles in the polymer matrix bulk as well as on surface with a perfect morphology. Evenly discrete Ag nanoparticles imbedded in PVA matrix are readily visible as black dots.
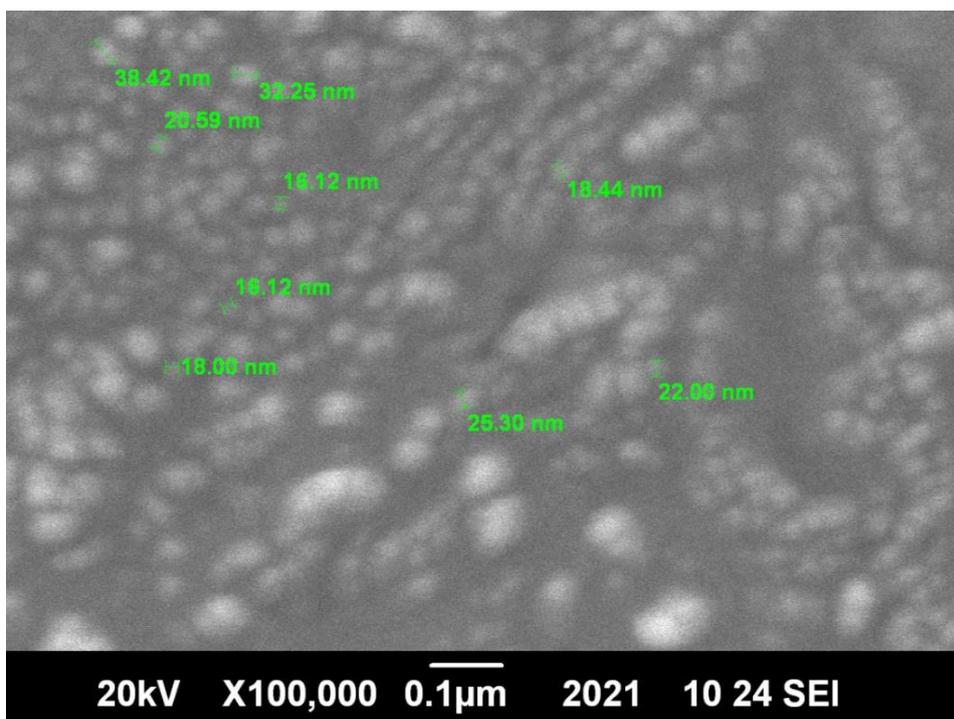

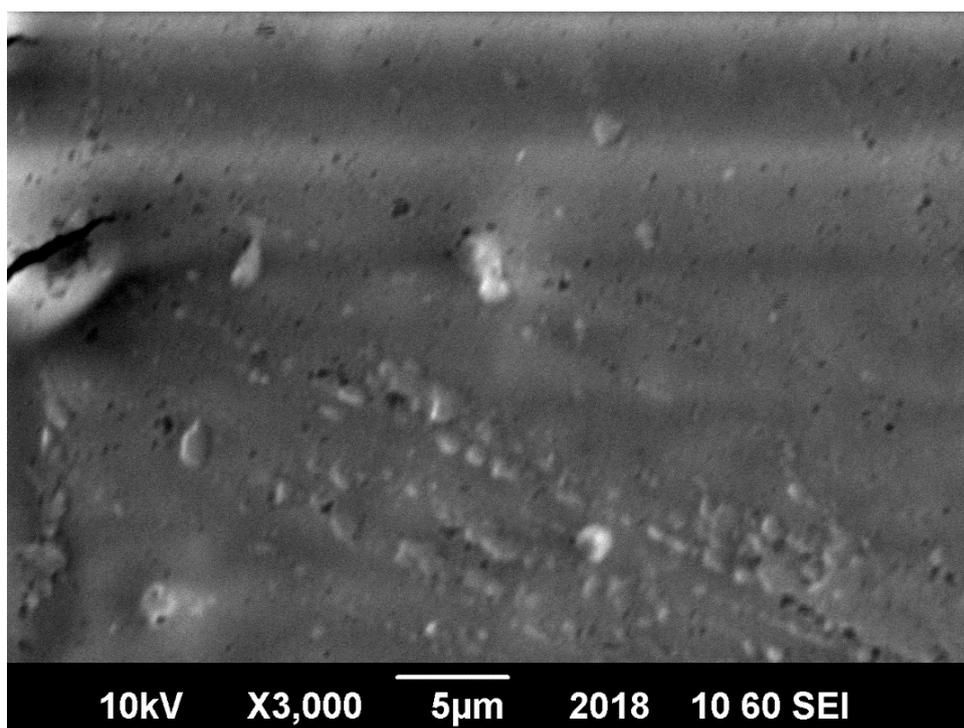**Figure 4: SEM image of the silver nanoparticles**

Figure 5: SEM image of Ag-PVA nanocomposite

4. Conclusion

The chemical reduction approach was used to successfully produce silver nanoparticles. Using the physical dispersion approach, these nanoparticles were successfully integrated into the poly (vinyl alcohol), resulting in a polymer-silver nanocomposite. The nanocomposite material was developed into uniform and smooth films, which were then characterized structurally and thermally. The XRD results indicate that the generated samples have a semi-crystalline structure, with the crystalline character of the material increasing as the amount of Ag nanoparticles rises. Thermal stability of the prepared material appears to upsurge with increasing amount of Ag nanoparticles filler according to TGA and DTA. SEM micrographs show consistently dispersed filler nanoparticles in matrix material, as well as a homogeneous topography of the films.

Acknowledgements

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