UV/VIS absorption properties of metal sulphate polymer nanocomposites

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In this study, the nanoparticles of $CaSO_4$, $SrSO_4$, and $BaSO_4$ were synthesized by precipitation method. Metal chlorides were used against the $(NH_4)_2SO_4$ for the synthesis of nanoparticles by using pure water and water-ethanol solvent system. The average particle size was calculated as 25.26/ 22.13 nm, 19.29/ 29.35 and 26.93 / 27.93nm for $BaSO_4$, $CaSO_4$ and $SrSO_4$ in ethanol-water/ pure-water system respectively. These nanoparticles were utilized for the preparation of PVAc nanocomposites films with 1-3 wt/wt% composition. These films were subjected to absorption of UV-Vis radiation and $SrSO_4$ composite found the best one for the absorption of UV light.

(Received August 20, 2021; Accepted December 1, 2021)

Keywords: UV-absorption, Metal sulfate nano particles, Polyvinyacetate nanocomposites

1. Introduction

Generation of materials at nanoscale has created a lot of applications in different areas of life. It has been observed that the materials which have dimensions in nanometer range possess the properties different from both those of atoms and bulk [1]. Research activities in the field of polymer nanocomposites for harvesting the solar energy grew very rapidly [2-4]. Various materials have been used to capture the maximum wavelength range of the solar spectrum [5, 6].

Numerous studies have been found to discuss the effect of $BaTiO_3$ addition in PVA to alter the dielectric/optical properties of the base material [7]. The only report regarding addition of bulk barium sulphate in polyvinyl alcohol was found for tuning of optical properties of the composite [8]. Typically, suplphates of Ba, Ca and Sr are recognized as some of the most promising candidates due to their chemical stability, nontoxicity [9], and high resistance to photo corrosion [10]. Nanoparticles of such metal sulphates combined with the polymeric materials may be used to tune the efficiency of photosensitive materials in an ecofriendly way [2, 11-14]. However reports on optical characterization of (Ba, Ca, & Sr)SO_4-PVAc nanocomposites remained limited so far. Therefore, the main aim of this work is to investigate the structure and optical characterization of PVAc with varied concentrations of sulphates of Ba, Ca and Sr nanoparticles, and making a comparison for best material in various applications [15].

2. Experimental

The mainly used raw materials were metal chlorides (calcium chloride, strontium chloride, and barium chloride), ammonium sulfate, sulfuric acid, water and chloroform which are purchased from local market. All these chemicals were used directly without any further purification. The particles were synthesized in water and ethanol as well.

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2.1. Synthesis of metal sulfate nanoparticles in water

The metal sulfate nanoparticles (metal = Ca, Ba, Sr) were prepared by direct chemical precipitation method. The equal molar ratio (0.1M, 20ml) of both the reagents (metal chlorides and sulfuric acid) were taken and their aqueous solutions were prepared separately. Subsequently, the sulfuric acid solution was added into metal chloride solutions drop wise in a round bottom flask under continuous and vigorous stirring at room temperature which continued for half an hour. Then, the mixture was left for precipitation process for further half an hour. After that, the white precipitates of metal sulfates were collected and washed with distilled water for several times using centrifuge machine. Finally, the sample was dried in an oven at 120°C for 12 hours and proceeded for characterization.

2.2. Synthesis of metal sulfate nanoparticles in ethanol

The metal sulfate nanoparticles (metal = Ca, Ba, Sr) were prepared in ethanol/water by precipitation method. The metal chlorides solution (0.5M, 20ml) and absolute ethanol (20 ml) were placed in a round bottom flask. Then, ammonium sulfate solution (0.1M, 10ml) was added drop wise into the reaction flask with continuous and vigorous stirring at room temperature for half an hour. Then, the mixture was kept for further half an hour to complete the precipitation process. After that, the white precipitates of metal sulfates were collected and washed with distilled water for several times using centrifuge machine. Finally, the sample was dried in an oven at 120 °C for 12 hours and proceeded for characterization.

2.3. Polyvinyl acetate / metal sulfates nanocomposites

The various nanocomposites of polyvinyl acetate were prepared by changing the nature of nanoparticles and their percentages by dispersion method along with pure PVAc as presented in Table 1.

Polyvinyl acetate (5g) was dissolved in absolute ethanol (50mL) and heated at 70 °C with constant stirring for 30 minutes. A clear homogenous solution (A) of PVAc was prepared. Metal sulfate nanoparticles (1%, 2%, & 3% by weight of PVAc) were dispersed in 10mL absolute ethanol and heated at 70 °C with constant stirring for 30 minutes. A suspension of nanoparticles was obtained and labeled as solution (B). For the preparation of mother solution, solution (B) was added drop wise in solution (A) with continuous stirring. The nanocomposites films were casted on aluminium plates and kept at 60 °C for four hours in an oven to remove the traces of solvent. The films were collected and proceeded for characterization.

Table 1. Polyvinyl acetate / metal sulfates nanocomposites.

Sr. No	Sample I.D	PVAc (g)	Nanoparticles (g)	Nanocomposites (%)
1	PVAc-0	5.0	0.0	Pure PVAc
Polyvinyl acetate / calcium sulfate nanocomposites				
2	F-C-1	4.95	0.05	1%
3	F-C-2	4.9	0.1	2%
4	F-C-3	4.85	0.15	3%
Polyvinyl acetate / strontium sulfate nanocomposites				
5	F-S-1	4.95	0.05	1%
6	F-S-2	4.9	0.1	2%
7	F-S-3	4.85	0.15	3%
Polyvinyl acetate / barium sulfate nanocomposites				
8	F-B-1	4.95	0.05	1%
9	F-B-2	4.9	0.1	2%
10	F-B-3	4.85	0.15	3%

3. Results and discussion

For the synthesis of nanoparticles, simple precipitation method was used. $BaSO_4$, $CaSO_4$ and $SrSO_4$ nanoparticles were synthesized by the use of two different solvent systems *i.e.* ethanol water system and pure water system. The results indicate that water-ethanol system is better than simple pure water for the synthesis of nanoparticles. In second step, nanoparticles which were synthesized in water-ethanol system were used for the synthesis of metal sulfate polymer nanocomposite films with different wt % of nanoparticles (1-3 wt%).

Figure 1 shows the FTIR spectra of $SrSO_4$, $BaSO_4$ and $CaSO_4$ nano- particles. FTIR spectra of indicate broad peaks about 3412 to 3523 cm^{-1} correspond to stretching mode of O—H group of $SrSO_4$ (A), $BaSO_4$ (B) and $CaSO_4$ nano- particles (C) which is contributed by the intra molecular hydrogen bonding (O—H …O). Peaks at 1630, 1634 and 1622 cm^{-1} show the deformation vibration of H_2O molecule $SrSO_4$, $BaSO_4$ and $CaSO_4$ nano- particles respectively. The absorption peaks in the region of 1411-1413 and 1307 cm^{-1} is due to the O—H bending vibrations internal face [11, 16].

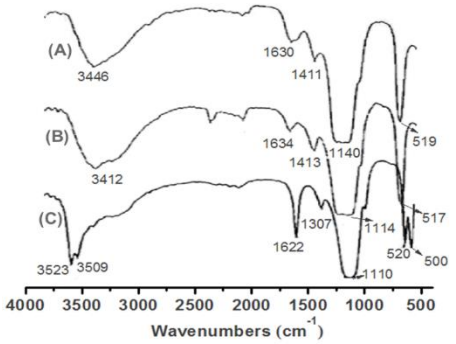

Fig. 1. FT-IR spectra of PVAc-$SrSO_4$ composite (A), PVAc- $BaSO_4$ composite (B) and bare PVAc (C).

Powered X-ray diffraction studies for the $BaSO_4$, $CaSO_4$ and $SrSO_4$ particles were done for two different solvents *i.e*. ethanol-water system (a1, b1, c1) and pure-water system (a2, b2 and c2). Figure 2 show the crystal data and the calculation of particle size with the help of Scherrer's formula, the particles of ($BaSO_4$, $CaSO_4$ and $SrSO_4$) synthesized in ethanol water system have average particle size of 25.26nm while for the particles synthesized in pure-water system the average size is 22.13nm [17].

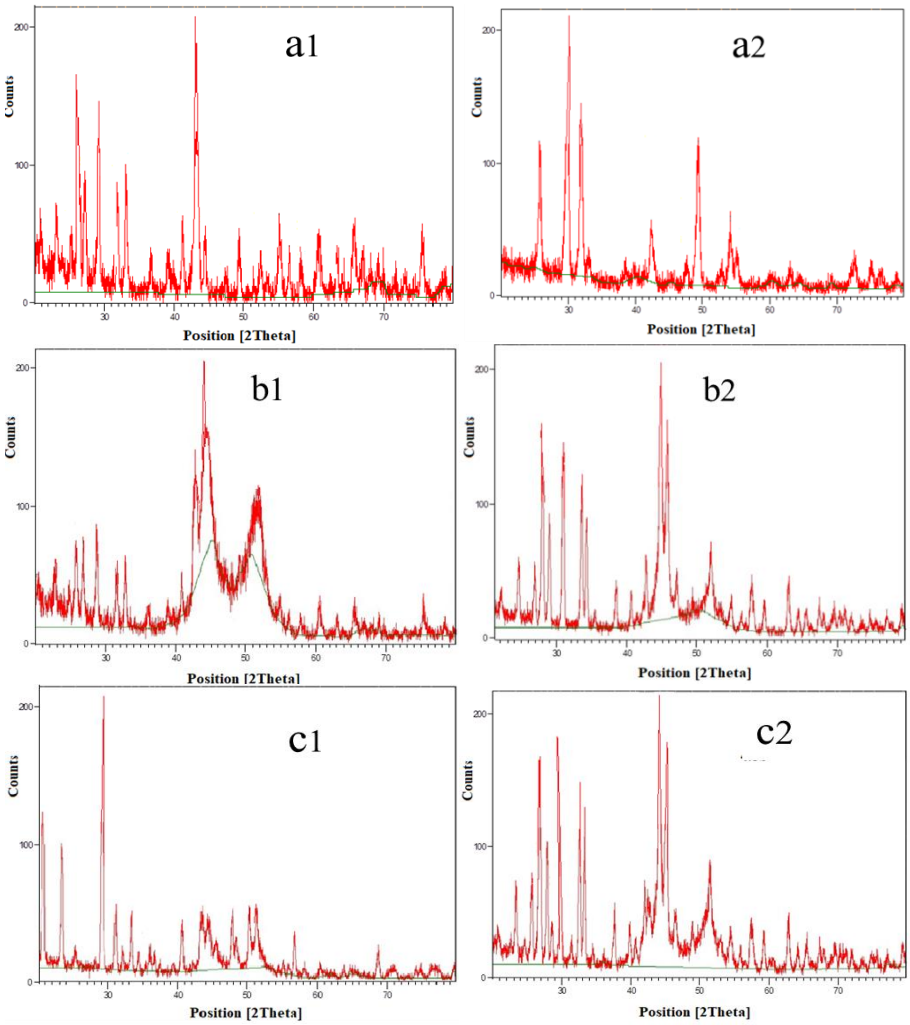

Fig. 2. XRD Spectra of $BaSO_4$ (a1,a2) $CaSO_4$(b1,b2) and $SrSO_4$ (c1,c2)

3.1. UV/Visible Absorption Data of PVAc & PVAc/ $BaSO_4$ nanocomposites thin films (1-3%)

The UV/Visible absorption studies of pure polyvinyl acetate (PVAc) and polyvinyl acetate-metal sulfate nano-composites were done. Figure 3 indicated the absorption of PVAc and PVAc/$BaSO_4$ nanocomposite films 1-3 wt% (F-B-1 to 3) respectively. From graph it is evident that maximum absorption is found in PVAc/$BaSO_4$ 2% (F-B-2). This result indicated that PVAc/$BaSO_4$ 2% nanocomposite show batter UV/Visible absorption properties by the addition of 2% barium sulfate nanoparticles as a filler instead of pure polyvinyl acetate.

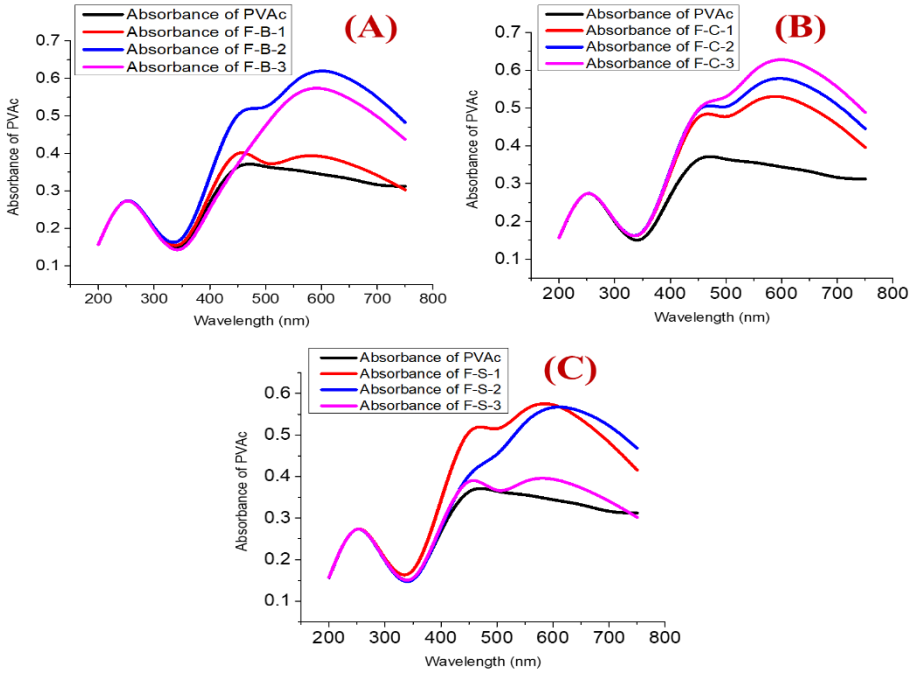

Fig. 3. Comparison of the absorption values of pure PVAc with $BaSO_4$ (F-B-1 to3) with $CaSO_4$ (F-C-1 to 3) and with $SrSO_4$ (F-S-1 to 3) Composite films.

The UV/Visible absorption studies of pure polyvinyl acetate (PVAc) and polyvinyl acetate-metal sulfate nanocomposites were done. Figure 3 shows the absorption of PVAc at different wavelengths. The maximum absorption (0.3858) is at λ_{max} 450. Figure 3(A) represents the absorption in case of PVAc/$BaSO_4$ nanocomposite films 1-3 wt% (F-B-1 to F-B-3) respectively against different wave lengths. Figure 3(A) shows the comparison of absorption values of pure PVAc and PVAc/$BaSO_4$ composite. From graph it is evident that maximum absorption is found in PVAc/$BaSO_4$ 2% (F-B-2). In this case λ_{max} is shifted from 450nm to 600nm compared with pure PVAc. This result indicates that PVAc/$BaSO_4$ 2% nanocomposite show batter UV/Visible absorption properties by the addition of 2% barium sulfate nanoparticles as a filler instead of pure polyvinyl acetate.

Figure 3(B) shows the absorption of PVAc at different wavelengths and PVAc/$CaSO_4$ composites 1-3 wt% (F-C-1 to F-C-3). From figure 3(B) it is evident that maximum absorption (0.6375) is found in PVAc/$CaSO_4$ 3% (F-C-3). In this case λ_{max} is shifted from 450 to 600 compared with pure PVAc. This result indicates that PVAc/$CaSO_4$ 3% nanocomposite show better UV/Visible absorption properties by the addition of 3% calcium sulfate nanoparticles as a filler instead of pure polyvinyl acetate. It is also evident from the graph that by the increased %age of nano filler, the UV/Visible absorption increases.

Similarly UV/Visible absorption studies of pure polyvinyl acetate (PVAc) and polyvinyl acetate-strontium sulfate nano-composites were done. Figure 3(C) shows the absorption of PVAc at different wavelengths. The maximum absorption (0.3858) is found at λ_{max} 450. Figures 3(C) shows the absorption in case of PVAc/$SrSO_4$ nanocomposite films 1-3 wt% (F-S-1 to F-S-3) respectively against different wave lengths. Figure 3(C) indicates the comparison of absorption in case of pure PVAc and PVAc/$SrSO_4$ composites. From figure 3 (C) it is evident that maximum absorption (0.581) is given by PVAc/$SrSO_4$ 1% (S-1). In this case λ_{max} is shifted from 450 to 600 compared with pure PVAc. This result indicates that PVAc/$SrSO_4$ 1% nanocomposite show better UV/Visible absorption properties instead of pure polyvinyl acetate. It is also evident from the graph that by the increased % age of nano filler, the UV/Visible absorption decreased. This point represents that very small quantity of strontium sulfate is required to alter the UV/Visible properties of pure polyvinyl acetate.

4. Conclusion

We have described the synthesis of barium sulphate, calcium sulphate and strontium sulphate nanoparticles through precipitation method by the use of two different solvent systems *i.e*. ethanol water system and pure water system. The average particle size of nanoparticles was calculated using Scherrer's formula and calculations indicate that the average particle size of $BaSO_4$ particles in ethanol-water and pure-water system was 25.26 nm and 22.13 nm respectively. The average particle size of calcium sulfate was 19.29 and 29.35 nm respectively in ethanol-water system and pure-water system. In case of strontium sulfate, the average size was 26.93 nm and 27.93 nm respectively. Results indicated that small particle size was obtained in case of ethanol water system. The presence of ethanol was helpful for the formation of small size particles. The nanoparticles synthesized in ethanol-water system were further exploited for the shifting of band gap from blue to red by embedding these particles in polyvinyl acetate thin films with 1-3 % wt/wt. The absorption property of pure PVAc film and PVAc nanocomposites films were studied with the help of UV/Visible spectrophotometer. 2% w/w composites films show batter UV/Visible absorption properties than pure polyvinyl acetate.

Acknowledgements

The authors gratefully acknowledge the support received for this research work from the Major Project of Fundamental and Application Research of the Department of Chemistry, School of Science, University of Management and Technology, Lahore, Pakistan and Office of Research Innovation and Commercialization UMT Lahore, Pakistan.

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