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SONOCHEMICAL SYNTHESIS OF STIBNITE NANOPARTICLES AND THEIR USE AS RADIOLYTIC STABILIZER IN POLYVINYL CHLORIDE MATRIX

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ABSTRACT

Stibnite (Sb_2S_3) was synthesized by sonochemical method. Amorphous powder of Sb_2S_3 was obtained and exhibit nanospheres structure with an average size in the range of 300-500 nm. Commercial Polyvinyl Chloride (PVC) containing Sb_2S_3 nanoparticles (PVC/Sb) at concentrations of 0.10; 0.30 and 0.50 wt% were investigated. The samples were irradiated with gamma radiation (^{60}Co) at room temperature and air atmosphere. The viscosity-average molar mass (M_v) was measured for PVC systems without nanoparticles and with nanoparticles. Decreases in molar mass observed when the systems were gamma irradiated reflect the random scission effects that take place in the main chain. Degradation index (DI) value was also obtained by viscosity analysis. DI results showed that the addition of Sb_2S_3 nanoparticles at 0.3 wt% into PVC matrix irradiated at dose of 25 kGy decreased the number of main chain scissions and was calculated a protection index of 66,5% in PVC matrix. Results about the free radical scavenger action of the Sb_2S_3 were obtained by use of 2,2-diphenyl-1-(2,4,6-trinitrophenyl)-hydrazyl radical (DPPH) and are discussed in this study. Changes in the infrared spectra of PVC systems indicated that polymer molecules interact with Sb_2S_3 nanoparticles.

INTRODUCTION

In recent years there has been considerable interest in nanoscale chalcogenides due to their remarkable properties and brilliant application prospects [1]. Among these materials, stibnite (Sb_2S_3) is well-known narrow band gap semiconductor that has attracted much attention.

A variety of chemical and physical methods have been developed to prepare sulfides. They were fabricated by gas-phase synthesis [2], by Bridgman method or gamma irradiation [3,4], micelles or monolayer surfaces [5,6], and in aqueous solvents [7]. In addition, template-mediated growth techniques have also been reported to synthesize sulfides nanoparticles with polymer materials [8]. However, most of the methods have some limitation in practice, especially the using of noxious compounds such as H_2S. Currently, sonochemical processing has been proving to be a useful technique for generating novel materials with unusual properties. Sonochemical arises from acoustic cavitation phenomenon: the formation, growth, and implosive collapse of bubbles in a liquid medium. The implosive collapse of the bubbles generates a localized hotspot, which has temperatures of about 5000°C, and very high

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pressures [9]. By using these extreme conditions, a series of materials have been synthesized [10].

PVC is a polymer widely used for radiosterilizable food packaging and medical devices. However when the polymer systems are submitted to sterilization by gamma radiation (25 kGy dose), their molecular structures undergo modification mainly as a result of main chain scission and crosslinking effects [11]. For PVC both processes coexist and either one may be predominant depending not only upon the chemical structure of the polymer, but also upon the conditions (temperature, environment, dose rate, etc.) under which irradiation is performed. The crosslinking and main scissions that take place during irradiation may lead to sharp changes in physical properties of the PVC [12, 13, 14]. Vinhas et al. [15] reported radio-protective action of a common photo-oxidative stabilizer, HALS (Hindered Amine Light Stabilizer), in PVC films plasticized with DEHP (di-2-ethylhexyl phthalate). The HALS additive is believed to interrupt oxidative propagation reaction by scavenging of chlorine radical formed in PVC radiolysis.

The preparation of polymer films containing disperse nanoparticles has a great interest. The importance of these nanocomposites is due the mechanical, electrical, thermal, optical, electrochemical, catalytic properties that will differ markedly from that of the component materials. In present investigation, we report the synthesis of Sb_2S_3 nanoparticles by sonochemical route under ambient air from solution containing antimony chloride as metal source and thioacetamide as a sulfur source. Films of PVC/nanoparticles were exposed to gamma irradiation and the effects of the nanoparticles on the viscosity average molar mass (M_v) of gamma irradiated PVC were studied. The modifications in the PVC structure by addition of nanoparticles were analyzed by infrared spectra. In addition the free radical scavenger action of Sb_2S_3 nanoparticles was discussed in this study.

EXPERIMENTAL

2.1 Synthesis and characterization of sulfide nanoparticles

All the reagents used in our experiments were of analytical purity and were used without further purification. Antimony chloride ($SbCl_3$) and thioacetamide (CH_3CSNH_2) were purchased from VETEC® (Brazil). Absolute ethanol and acetone were purchased from DINAMICA® (Brazil).

In typical procedure, 0.45 g of $SbCl_3$ and 0.8 g of thioacetamide (CH_3CSNH_2) were dissolved in 50 mL of absolute ethanol in becker of 100 mL. Then the mixture solution was exposed to ultrasound irradiation under ambient air for 0.5 h. Ultrasound irradiation was accomplished with a high-intensity ultrasonic probe (Sonic, 20 kHz, 500 W) immersed directly in the reaction solution. When the reaction finished, a red precipitate was obtained. After cooling of the sample to room temperature, the precipitate was separated by centrifuging, washed with absolute ethanol, distilled water, and acetone in sequence. Then the precipitate was dried in a desiccator at room temperature for 24 h. The final product was characterized by Scanning Electron Micrograph (SEM) and X-ray diffraction (XRD). The

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SEM patterns were taken on a JEOL JSM- 5900 Scanning Electron Microscopy, and XRD patterns were taken on a Siemens D5000 Diffractometer equipped with graphite monochromatized CuKα radiation (λ=1.5418Å) using employing a scanning rate of 0.02 deg/s in the 2θ range from 10 to 70°.

2.2 Preparation of PVC/nanoparticles films

The studied polymer material was commercial PVC (Tiletron, Brazil). The films of PVC and PVC with addition of sulfides were prepared by solvent-casting from methyl-ethyl-ketone (MEK) solvent by slow evaporation in air at room temperature (≈ 27ºC) upon 48h of magnetic stir of the polymer solution (1,8g of the PVC/40 mL of the MEK). MEK was dried with Na_2SO_4 and purified by distillation. In this study the PVC/nanoparticles films are named PVC/Sb for PVC+ Sb_2S_3 systems. The concentrations of nanoparticles used in this study were 0.10; 0.30; 0.50 and 0.70 wt%.

2.3 Viscosity measurements

The viscosity measurements of PVC and PVC/Sb films were carried out in tetrahydrofuran (THF) solution at 25.0 ± 0.1°C using an Ostwald viscometer in a thermostatic bath. The intrinsic viscosity of the samples was calculated from the relative viscosity, $\eta_{rel} \approx \nu/\nu_0 \approx t/t_0$, within range of 1.1 – 1.9, where ν and ν_0 are the cinematic viscosities on the polymer solution and the solvent, respectively. The t and t_0 are flow times of solution and solvent, respectively. Therefore, η_{rel} was calculated from t/t_0 ratio. The specific viscosity ($\eta_{sp}= \eta_{rel} - 1$) and the reduced viscosity ($\eta_{red} = \eta_{sp}/C$), where C is the concentration of the solution (0.6 g/dL), were calculated as well. The intrinsic viscosity [η] was determined by the Solomon-Ciuta equation [16]:

$$[\eta]= (2^{1/2}/C) (\eta_{esp} - \ln \eta_{rel})^{1/2} \quad (1)$$

Then the viscosity average molar mass, M_v, was calculated from the corresponding [η] values trough the Mark-Houvink equation [17]:

$$[\eta] = K M_v^{a} \quad (2)$$

Where K and a are 1.5 x 10^{-4} dL/g and 0.766, respectively for the THF-PVC system at 25°C [18].

Radiostabilizing action of Sb_2S_3 on PVC matrix can be assessed by comparison of degradation index parameter (DI), $DI=(M_{vo}/M_v)–1$, for a determined irradiation dose. The M_{v0} and M_v are the viscosity average molar mass before and after the gamma irradiation, respectively. DI is obtained from viscosity analysis and reflects the number of main chain scissions per original molecule after irradiation.

2.4 Irradiation of samples

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PVC and PVC/Sb films were exposed to gamma radiation from a ^{60}Co source (dose rate of 6.13 kGy/h) at dose of 25 kGy (sterilization dose) in presence of atmosphere air and at room temperature (≈ 27ºC).

2.5 Free radical scavenger action of the nanoparticles

2,2-diphenyl-1-(2,4,6-trinitrophenyl)-hydrazyl radical (DPPH) solution was prepared using ethanol as solvent. Was dissolved 0.0024g of the DPPH in the 100 mL ethanol. Appropriate amount of Sb_2S_3 were mix with the DPPH solution and the mixture must be vigorously agitated. The reaction was carried out at ambient temperature for 30 min. The absorbance at 515 nm was measured against a blank of pure ethanol after the reaction in a UV-vis spectrophotometer Spectro 22, 108-D and 60 Hz. Radical DPPH scavenging capacity (%SC) was estimated from the difference in absorbance with or without nanoparticles (equation 3).

$$\%SC=(A_s - A_{sn})x\ 100 \quad (3)$$

Where A_s=DPPH solution absorbance and A_{sn}=DPPH solution absorbance for system with sulfide nanoparticles. All tests were conducted in triplicate.

2.6 FT-IR characterization

The infrared spectra of PVC and PVC/Sb films were obtained by Fourier Transform Infrared Spectroscopy (FT-IR). The analyses were carried out on Brucker-IFS66 equipment in the transmittance mode in 4000-400 cm^{-1} frequency region, the number of scans was 75 with resolution of 4 cm^{-1}, and KBr pellets.

RESULTS AND DISSBSSIONS

3.1 Sulfide nanoparticles characterization

The Sb_2S_3 nanoparticles were obtained with successful by sonochemical method proposed in this study. The synthesis of the Sb_2S_3 was carried out in ethanol as a solvent. The synthesis carried out at room temperature, during 30 min of the sonication using 500 W (100% of machine power). This method is very fast and very simple. For ultra sonic irradiation were found two main effects. The first, favored the dissolution of the thioacetamide and the formation of S^{2-}, thus accelerating the reaction, and the second prevented the aggregation of the resulting nanoparticles. During the sonication, bubble collapse in liquid resulted in an enormous concentration of energy from the conversion of kinetic energy of the liquid motion into heating of the contents of the bubble. The high local temperature and pressure provide favorable conditions for driving the decomposition of the metal/thioacetamide complex, giving rise to the formation of sulfides. It has been known that there are two regions of sonochemical activity [19]. One is the inside of the collapsing bubbles, where elevated temperature and high pressures are produced. The other is the interfacial region between the cavitation bubbles and the surround bulk solution. Though the temperature in the interfacial region is much lower than interior of the collapsing bubbles, it is still high enough to rupture chemical bonds and induce a variety of reactions. If the reaction takes place inside the

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collapsing bubbles, the product obtained is amorphous as a result of the extremely rapid cooling rate, which occurs during collapse. On the other hand, if the reaction takes place within the interfacial region, one would expect to get nanocrystalline products [19, 20, 21]. The more uniform distribution dispersion of the nanoparticles, a marginally higher surface area, better thermal stability, and phase purity, are some of the advantages of the preparation of sulfide nanoparticles by sonochemistry method.

The Fig. 1 shows the XRD patterns and SEM images of Sb_2S_3. No diffraction peak was detected in the XPRD pattern of Sb_2S_3 (see Figure 1a), indicating that the antimony sulfide powder was amorphous. Since amorphous Sb_2S_3 powder was obtained, we propose that the formation of this nanoparticle probably occurs inside the collapsing bubbles formed during sonication. The SEM image (Figure 1b) showed that the amorphous Sb_2S_3 is composed of monodiperse nanospheres, whose diameters were calculated in the range of 300-500 nm.

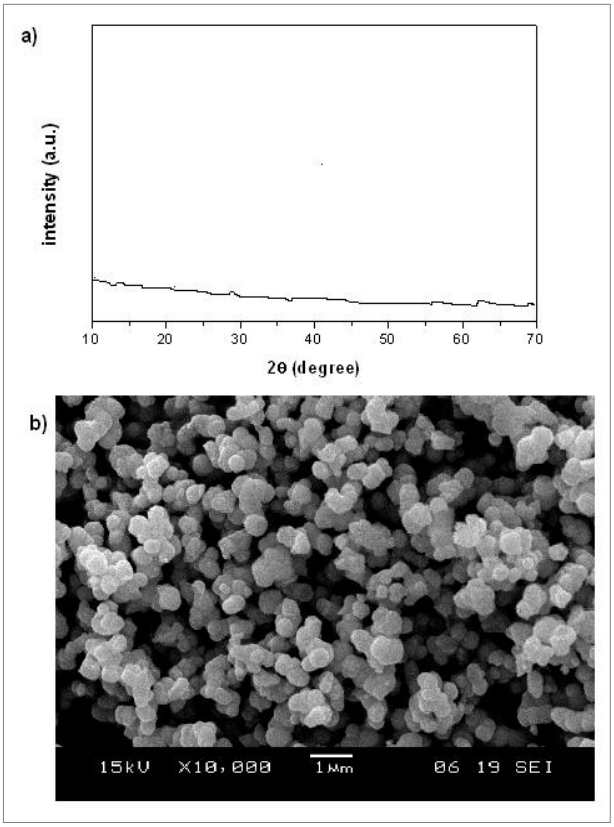

Figure 1. a) XRD pattern of the SbS nanocrysltal;
b) SEM image of SbS

3.2 Radiolytic action of nanoparticles in PVC matrix

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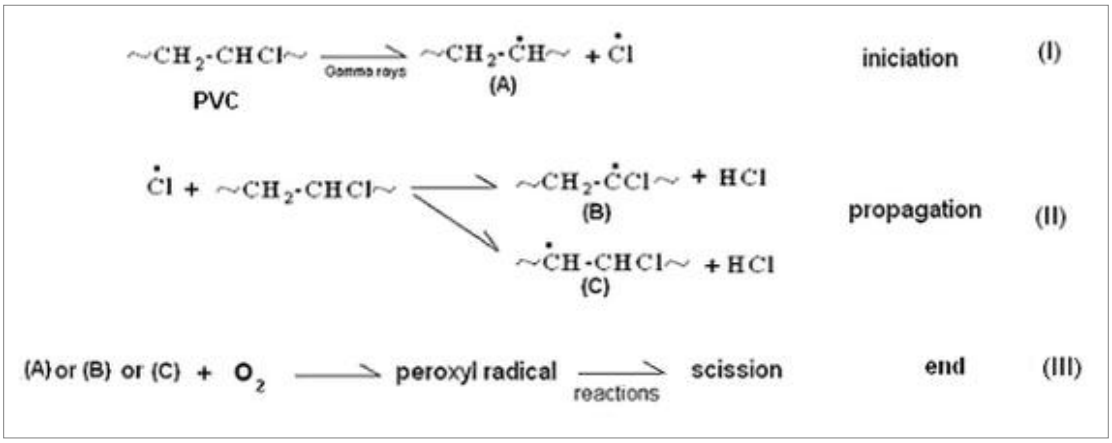
When PVC was exposed to gamma radiation its Mv decreased from 101298± 2233 to 91150 ± 1158, which characterizes the main chain scission effect. This result agrees with literature reports about the effect of gamma radiation on the PVC matrix [12, 14, 15].

During the interaction of gamma radiation with PVC, the reactions shown in scheme 1 can take place [14]. This interaction gives rise to macroradicals deriving from C-Cl bond scission reactions (reaction I) [11]. The chlorine radical continues the reaction by way of a form center reaction in which HCl is formed and acts as a catalyst (reaction II). However in presence of air the polymeric radicals A, B and C react with oxygen from air producing the peroxyl macroradical (reaction III). This radical formed can them undergo further reactions leading to main chain scission. This effect is predominant when the PVC molecule is irradiated at 25kGy as shown in Table 1for all systems.



Scheme 1. Radiolytic degradation mechanism of PVC molecule

Table 1 shows M_v for the PVC/Sb before and after irradiation. Note that M_v also decreases in irradiated samples of films. However the analysis of Tables 1 revealed less chain scissions occur in PVC/Sb films at 0.30 wt% concentration. At sterilization dose (25 kGy) we calculated DI = 0.111 for PVC and DI = 0.037 for PVC/Sb samples. These data represent a decrease of 67% in scissions per original molecule of PVC. In addition, with the increase of concentration of the nanoparticles in the PVC matrix was observed a decrease of the stabilizing action of nanoparticle on the systems. The probable explain is the impurity action of nanoparticle on the system.

No information about use of Sb_2S_3 in the radiolytic stabilization of polymers has been published and consequently the mechanism of radiolytic stabilization effect of these nanoparticles is not clear. However, some probable reactions may be going on under gamma irradiation.

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The gamma rays can break covalent bonds in PVC molecule to directly produce the free radicals as was shown in Scheme 1 (I and II). The gamma rays can also produce excited states in PVC which undergo further reactions to produce the A radical (Scheme 1) indirectly.

The efficiency of certain composts in the stabilization of polymer molecules against radiation may be evaluated by measuring the effect of these composts on the free radical population after irradiation, as well as on its rate of decay. The Table 2 shows the results obtained by use of Sb_2S_3 nanoparticles as a scavenger free radical on the DPPH solution.

Table 1. Viscosity results obtained for PVC/Sb

Concentration of SbS (wt%)	Dose (kGy)	M_v (g/mol)	DI	Protection (%)
0.10	0 25	106810±2233 91150±1158	0.054	51
0.30	0 25	106012±1452 102198±918	0.037	67
0.50	0 25	109896±1231 103044±1616	0.067	40
0.70	0 25	106263±1965 95231±1499	0.116	0

DPPH is a stable free radical, non natural, whose properties differ from the highly reactive oxygen radicals such as the hydroxyl, alkoxyl and superoxide. Looking at this structure (Scheme 2 step I) it is expected that DPPH can react with another free radical in several different ways: i) by coupling to the nitrogen-centered radical (structure A); ii) by coupling in the para-position on the phenyl ring (structure B), and iii) coupling somewhere on the picryl moiety (structure D). Thus, the DPPH free radical scavenging assay presents itself as a test of prediction of the antioxidant potential activity. The assay is grounded on the DPPH property of presenting a strong absorption at visible spectrum in wavelength of 515 nm, characterized by an intense violet coloration, due to the presence of free electrons. When the DPPH is in the presence of substances able to scavenge free radicals, the absorption is inhibited, leading to a stoichiometric discoloration in relation to the number of reduced molecules of DPPH. The degree of discoloration is directly correlated with the free radical scavenger activity of the evaluated substance [22, 23].

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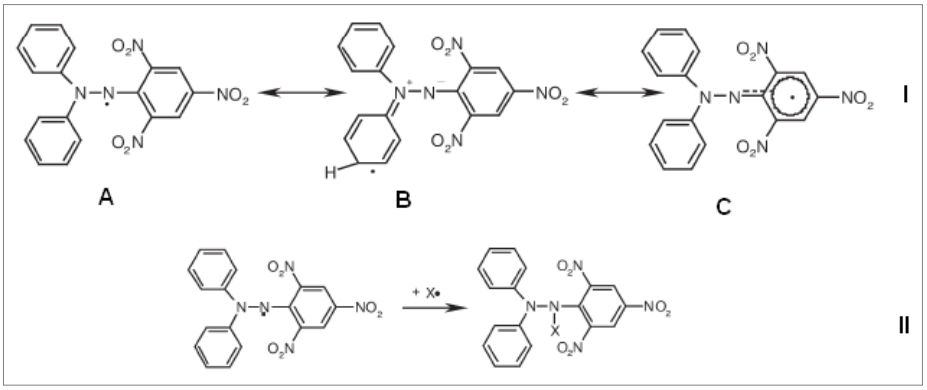
Table 2 Radical DPPH scavenging capacity (SC) results

System	absorbance	SC (%)
DPPH	0.83 ±0.02	-
Sb_2S_3	0.34±0.08	60

Ours results reveal that nanoparticles in the amount of 0.0054g (equivalent to concentration of 0.3 wt% in PVC matrix) have scavenger free radical action and explain the radiolytic protection action on PVC matrix. The Sb_2S_3 presented scavenger activity with 60% of free radical capture.



Scheme 2. Capture mechanism of DPPH free radical

The results obtained by DPPH tests agrees with viscosity results and is satisfactory considering the small amount of Sb_2S_3 added to the system. Thus the nanoparticle used in this study may be considered as an additive with stabilizing action on the PVC molecules. Due the small amount of nanoparticles dissolved in the DPPH solution is expected a formation of ions in the system. There are two ways in which DPPH can react with an anion and explain our results: i) the anion acts as a nucleophile and makes a Meinseinhaimer complex (scheme 2 compound D), which decomposes after that by losing a hydride anion or a nitrite anion, or ii) the DPPH radical is strong enough to abstract one electron from the anion and to oxidize it to the short-lived radical $x^{\cdot}$, which reacts with DPPH in the same way shown in Scheme 2 step II, yielding also finally the nitro derivative of DPPH [24,25].

The chain property species in autoxidation caused by oxygen action on PVC radical formed by gamma irradiation are peroxy radicals (scheme 1) and an effective inhibitor must interrupt these chains. We assumed the free radical scavenge to be the principal function of the

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nanoparticles on the films of PVC, but further work to require to providing a better understanding of all processes involved in the radiolytic action of the nanoparticles on PVC matrix.

3.3 FT-IR analysis

The FT-IR spectroscopy has used to detect and identify the presence of intermolecular interactions occurring between PVC molecule and Sb_2S_3 nanoparticles. Figure 3 shows FT-IR spectra of PVC and PVC/Sb for non-irradiated films in 4000-400 cm^{-1} frequency region. The 700-600 cm^{-1} frequency region may be used in order to determine the existence of specific interactions in PVC/Sb. This frequency region is attributed to C-Cl stretching vibration in PVC molecule [26]. The comparison of spectra showed which PVC frequency region is shifted from a double peak in 698 and 622 cm^{-1} to a single peak in 650 cm^{-1} with addition Sb_2S_3 in the system. This result indicates that strong intermolecular interactions exist between the PVC and Sb_2S_3 nanoparticles. The changes in PVC/Sb spectrum suggest that the adsorption of nanoparticles on PVC molecules occurs near to Cl group. In addition one signal at 1716 cm^{-1} assigned to carbonyl group (C=O) was found in both PVC spectrum and PCV/Sb spectra. The carbonyl group may be attributed to plasticizers which are associated with PVC molecules in industrial processes and structural defects like ~$COCHClCH_2$~ which are common in commercial PVC. Similar results were found in irradiated films and are not presented in this paper.

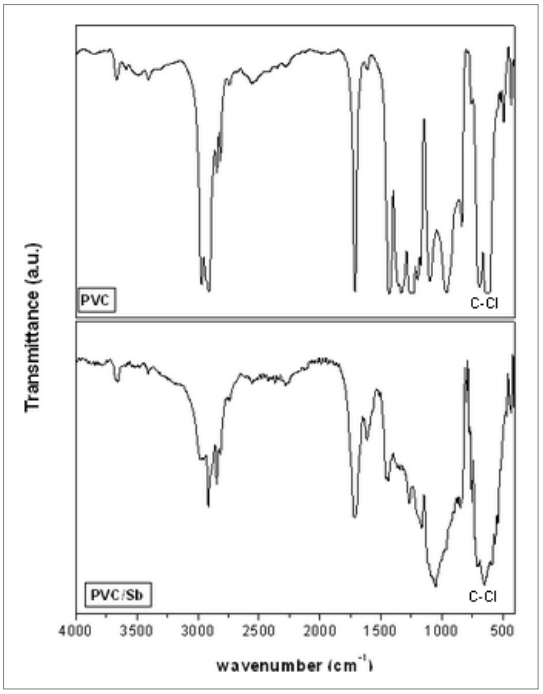

Figure 3. FT-IR spectra of PVC and PVC/Sb films for non irradiated films

CONCLUSIONS

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The Sb_2S_3 nanoparticles were successful synthesized through sonochemical method. The Sb_2S_3 nanoparticles exhibited amorphous morphology. The nanoparticles were added in PVC matrix to form PVC/nanoparticles films. The viscosity analyses suggest that nanoparticles (0.3 wt%) protected PVC against radiolysis by free radical scavenging mechanism. Changes in the FT-IR spectra of PVC/Sb were detected indicating strong interactions between PVC molecule and Sb_2S_3 nanoparticles.

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