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SONOCHEMICAL SYNTHESIS OF COOPER II SULFIDE NANOPARTICLES AND THEIR USE AS RADIOLYTIC STABILIZER IN POLYVINYL CHLORIDE MATRIX

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ABSTRACT

Cooper (II) sulfide (CuS) was synthesized by sonochemical method. CuS crystals with hexagonal structure exhibit irregular aggregates of particles with an average size in the range of 250-900 nm. Commercial Polyvinyl chloride (PVC) containing CuS nanoparticles (PVC/CuS) at concentrations of 0.10; 0.30; 0.50 and 0.70 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. Decrease in viscosity molar mass was 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 CuS nanoparticles at 0.5 wt% into PVC matrix decreased the number of main chain scissions at dose of 25 kGy and was calculated a protection of 84% in PVC matrix. CuS nanoparticles act as free radical scavenger into gamma-irradiated PVC systems. The interactions between CuS and PVC favor action of nanoparticles as a good plasticizer in the PVC molecule.

1. 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, cooper (II) sulfide (CuS) 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 pressures [9]. By using these extreme conditions, a series of materials have been synthesized [10].

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PVC is a polymer widely used for food packaging and medical devices sterilized by gamma irradiation. 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]. Both processes coexist for PVC molecules 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 like 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 CuS has of a great interest. The importance of these composites 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 CuS nanoparticles by sonochemical route under ambient air from solution containing cooper (II) 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 CuS and mechanical properties of PVC/nanoparticles films were discussed in this study.

2. 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. Cooper (II) chloride ($CuCl_2$) and thioacetamide (CH_3CSNH_2) were purchased from VETEC® (Brazil). Absolute ethanol and acetone were purchased from DINAMICA® (Brazil).

In typical procedure, 0.50 g of $CuCl_2$ and 0.45 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 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 desiccator at room temperature for 24 h. The final product was characterized by Scanning Electron Micrograph (SEM) and X-ray diffraction (XRD). The 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°.

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2.2 Preparation of PVC films

The studied polymer material was commercial PVC (BRASKEM, Brazil). The films of PVC and PVC with addition of CuS 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/CuS for PVC + CuS systems. The concentrations of nanoparticles used in this study were 0.10; 0.30; 0.50 and 0.70 wt%. The films were characterized by JEOL JSM-5900 Scanning Electron Microscopy (SEM).

2.3 Viscosity measurements

The viscosity measurements of PVC and PVC/nanoparticles films were carried out in 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]:

$$[\eta] = \frac{1}{C}\sqrt{2(\eta_{sp} - \ln\eta_{rel})} \quad (1)$$

Then the viscosity average molar mass, M_v, was calculated from the corresponding [η] values trough the Mark-Houwink 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 sulfide nanoparticles on PVC matrix can be assessed by comparison of degradation index parameter (DI), $DI=(M_{v0}/M_v)–1$, 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

PVC and PVC/nanoparticles 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).

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2.5 Freeradical 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 sulfide nanoparticles 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).

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

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 Mechanical properties

The tensile properties of the films were determined according to ASTM D-882 using an Instron machine IMIC, DL-500 N. The crosshead speed was 10 mm/min. The tests were carried out at room temperature (≈ 27ºC) and the results shown in this study are an average of four samples.

3. RESULTS AND DISCUSSIONS

3.1 Sulfide nanoparticles characterization

The CuS nanoparticles were obtained with successful by sonochemical method proposed in this study. The synthesis of the CuS 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 ultrasonic 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 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

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within the interfacial region, one would expect to get nanocrystalline products [19, 20]. 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.

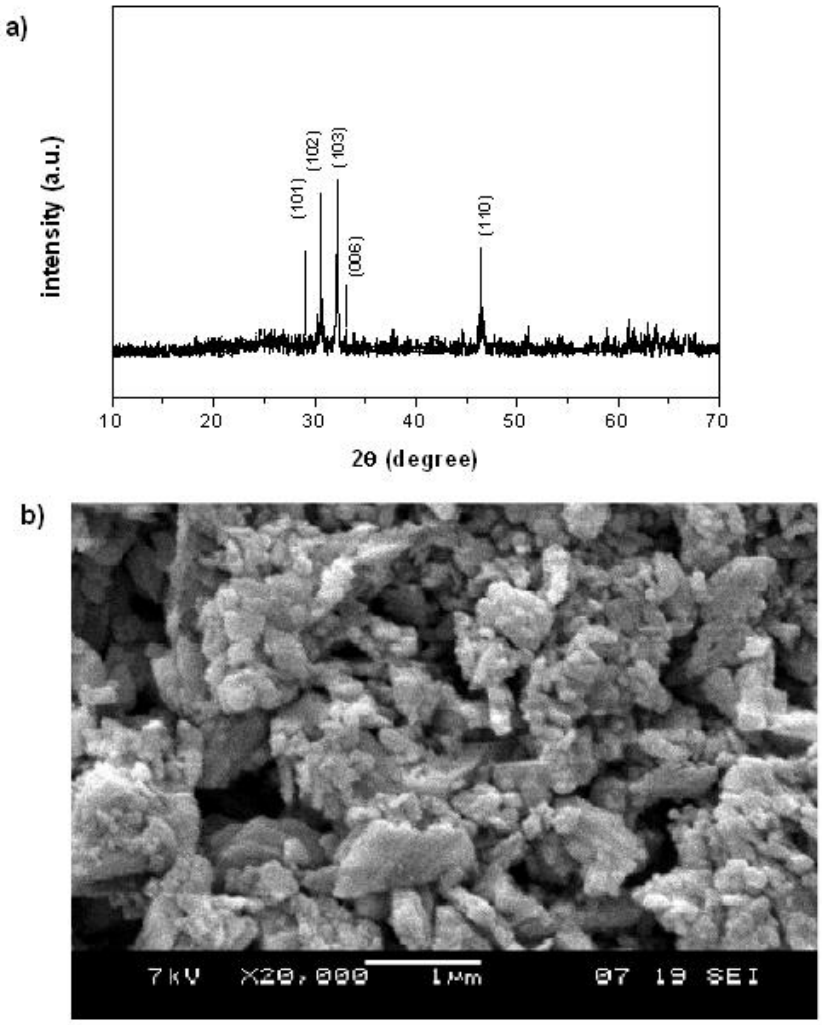

Figure 1. Analyses of CuS for a) XRD pattern and b) SEM image

The Fig. 1 shows the XRD patterns and SEM images of CuS. According to the JCPDS card (JCPDS n° 65-3928), the phase of the CuS showed in Fig. 1a, can be indexed to be a hexagonal structure which is consistent with results reported in the literature [21]. No other characteristic peaks of impurities were detected. These results demonstrate that CuS with high chemical purity have been synthesized using sonochemical method. The morphology and size of the CuS were analyzed by SEM observations. The Fig. 1b is SEM image of the CuS and it was observed that the CuS crystals are composed of particles aggregates with irregular forms. The size of the particles aggregates was found in the range of 250-900 nm, i.e. the

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synthesized CuS is in nanometer scale. The SEM image also showed that the CuS was agglomerated to some extent. This is probably due to the drying artifact used during the preparation of the grid for SEM imaging.

3.2 PVC/CuS films

SEM images of PVC with CuS at studied concentrations were obtained and showed similar behavior with homogeneous dispersion of nanoparticles in the polymer matrix. The Figure 2 is an example and shows the SEM images of PVC with CuS at 0.5 wt%. The Figure 2a shows that PVC film is compact homogeneous material presented a compressed assembly of flat globular particles. On the other hand, analyzing the Figure 2b (PVC/Cu film) is observed that the system is already quite homogeneous and did not require the addition of the dispersing agent for better dispersion of Cu nanoparticles in the PVC matrix. The SEM images of irradiated nanocomposites presented similar behavior than unirradiated SEM images and not are shown in this paper.

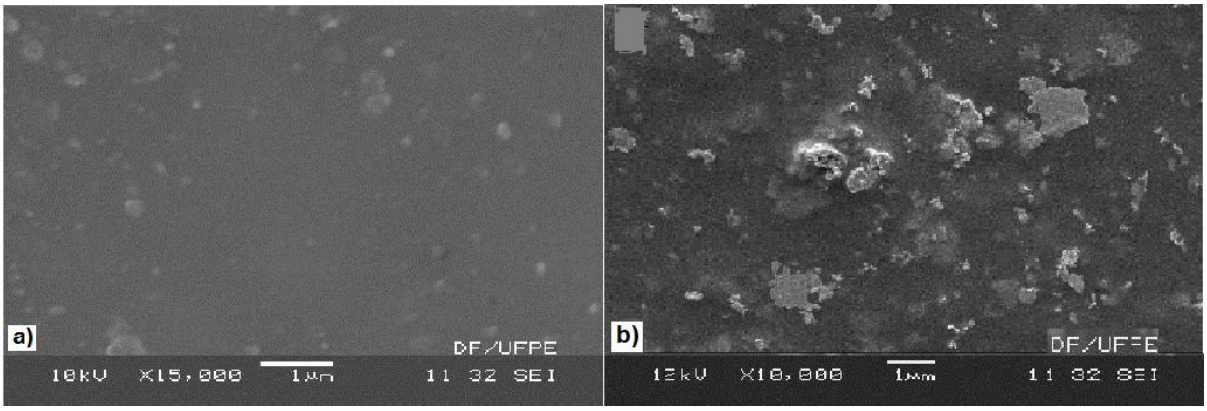

Figure 2. SEM images of a) PVC and b) PVC/CuS

3.3 Radiolytic action of nanoparticles in PVC matrix

When PVC was exposed to gamma radiation its Mv decreased as showed in Table 1 and the DI value found was 0.126. These results characterize the main chain scission effect in the PVC molecule and agree with literature reports about the effect of gamma radiation on the PVC matrix [12, 14, 15].

The Scheme 1 represents the radiolytic degradation of PVC [22]. Selective scission of C-Cl bond to produce polymer radical A may be expected in reaction I because the this bond dissociation energy is 20 kcal/mol less than of the C-H bond [23]. The chlorine atom formed in reaction I then attacks the adjacent methylene group to regenerate the radicals B or C in reaction II. However, evidence from the chlorination of aliphatic chlorides suggests that attack on the methylene group that to form C radical is preferred [24]. The radical C is in contrast to radical A or B, because is quite unstable and can undergo a spontaneous

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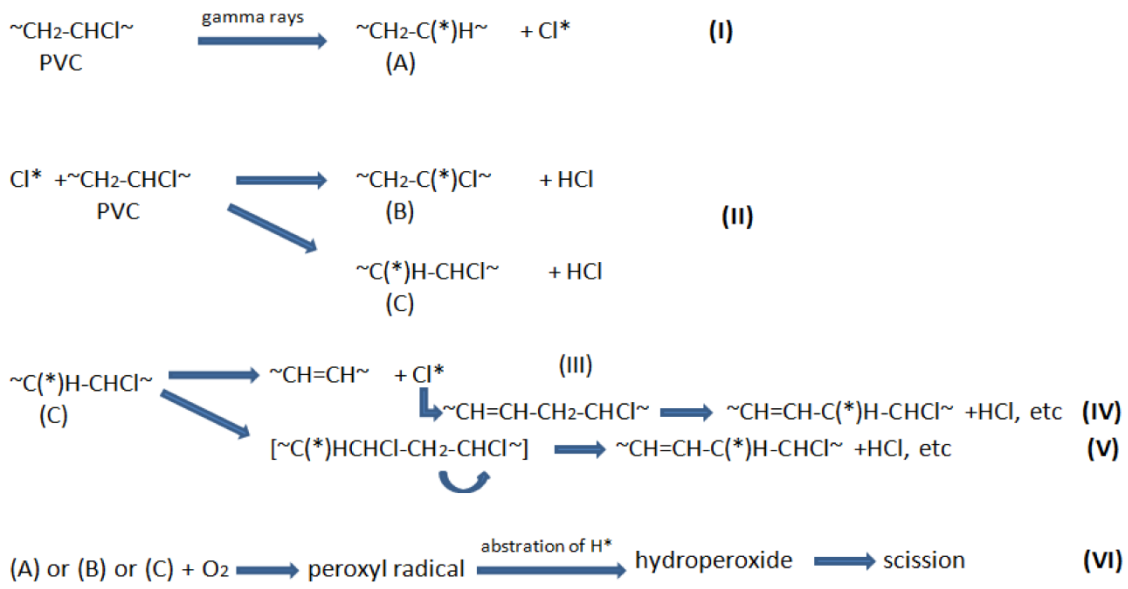
dissociation (reaction III). Thus, a chain reaction from radical C leading to the formation of HCl and conjugated instauration is propagated (reactions IV). It is possible that this propagation may not involve a free Cl atom, but rather a simultaneous dissociation and abstraction conform is showed in reaction V [22].

The Table 1 shows M_v for the PVC/CuS before and after irradiation. Note that M_v also decreases in irradiated samples. However the analysis of this Figure revealed less chain scissions occur in PVC/CuS films at concentrations of 0.3; 0.50 and 0.70 wt%. The better result was obtained for 0.5 wt% concentration and at sterilization dose (25 kGy) we calculated DI = 0.020 for PVC/CuS film. These data represent a decrease of 84% in scissions per original molecule of PVC. This result showed a great radiolytic stabilization of CuS in the PVC matrix. 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. At concentration of 0.7 wt% the protective action of CuS decreased to 64%. The probable explain is the CuS in the determined concentration begins to hydroperoxide decomposition [25], which can promotes the PVC degradation as was showed in Scheme 1, reaction VI, i. e., high concentration of CuS losses its radiolytic stabilization action.



Scheme 1. Radiolytic degradation mechanisms of PVC molecule [22]

No information about use of CuS 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. The gamma rays can break covalent bonds in PVC molecule to directly produce

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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 CuS nanoparticles as a scavenger free radical on the DPPH solution.

Table 1. Viscosity results obtained for PVC/CuS

Concentration of CuS (wt%)	Dose (kGy)	M_v (g/mol)	DI	Protection (%)
0.0	0 25	63874±1399 56732±1767	0.126	-
0.1	0 25	81822±2044 71578±2399	0.143	-
0.3	0 25	78084±3022 71618±3900	0.090	29
0.5	0 25	75182±2867 73719±2484	0.020	84
0.7	0 25	82337±2097 78824±1925	0.045	64

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 [26].

Table 2 Radical DPPH scavenging capacity (SC) results

System	absorbance	SC (%)
DPPH	0.83 ±0.02	-
CuS	0.46±0.07	45

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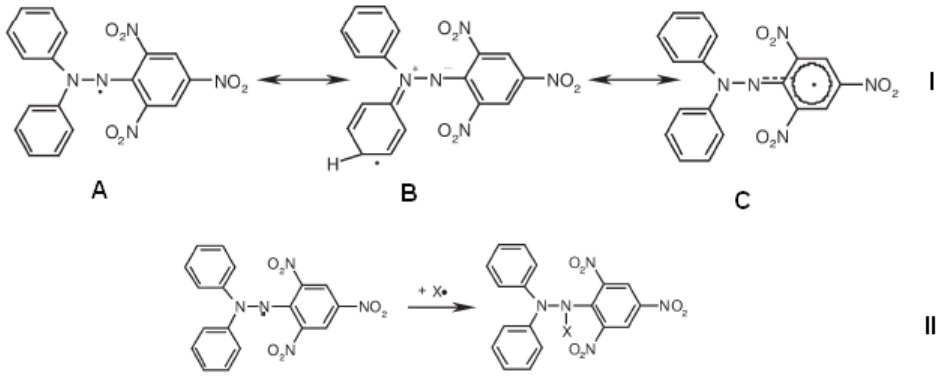
Ours results reveal that nanoparticles in the amount of 0.0090g (equivalent to concentration of 0.5 wt% in PVC matrix) have scavenger free radical action and explain the radiolytic action on PVC matrix. The CuS presented scavenger activity with 45% of free radical capture.



Scheme 2. Capture mechanism of DPPH free radical [26]

The results obtained by DPPH tests agrees with viscosity results and is satisfactory considering the small amount of CuS 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 [27,28].

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 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.

3.5 Mechanical properties

The results of mechanical measurements for PVC and PVC/CuS (0.5 wt%) are summarized in Table 3 for irradiated and unirradiated samples. The properties studied were Elongation at break (Eb) and Young´s modulus (Ym).

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Analyzing the unirradiated systems was found that the value of Ym for PVC/CuS decreases 27% when compared with the Ym value of PVC. This result means a decrease in rigidity of the PVC and consequently explains the increase of 45% on Ea value of PVC/CuS. Thus, the CuS nanoparticles act also as a plasticizer in the PVC molecule. The possible explication is that PVC shows dipole-dipole attraction as a result of the electrostatic interactions between the chlorine atom of one polymer chain (negative pole) and the hydrogen atom of another polymer molecule (positive pole). These interactions could be weakened by strong intermolecular interactions between PVC and CuS, which promote decrease in the density of entanglements points of the polymer molecules. This effect increasing the polymer flexibility, decreasing the Ym value and consequently increase the Eb values.

For the films of PVC irradiated at 25 kGy was found a decrease of 26% in Ym value with consequent increase in Eb value. The chain scission effect obtained by gamma irradiation (Table 1) provokes the decrease of average length of PVC molecule. The density of entanglements points decreases leading to a decrease of the Ym value as consequence of PVC radiolytic degradation. The lower molecular weight also makes fibrils less stable and therefore favors brittle fracture [17]. On the other hand, a decrease of 16% in Ym value and not significant change in Eb values were found for irradiated PVC/CuS. These results are explained by stabilizer action of CuS in the PVC matrix and agree with the viscosity measurements.

Table 3. Effects of nanoparticles and gamma irradiation in the mechanical properties of PVC

	Dose (kGy)	**Ym (MPa)**	**Ea (%)**
PVC	**0**	913.33 ±82.24	7.43±0.83
	25	674.23±61.08	8.89±0.43
PVC/CuS	**0**	664.95±77.84	10.79±0.56
	25	557.45±88.51	9.88±0.39

4. CONCLUSIONS

The CuS nanoparticles were successful synthesized through sonochemical method and exhibited crystalline morphology and aggregates at the nanoscale. The CuS nanoparticles were added in PVC matrix to form PVC/CuS films. The viscosity analysis suggests that CuS nanoparticles at 0.5 wt% concentrations protected the PVC against radiolysis by free radical scavenging mechanism. The interactions between CuS and PVC favor action of nanoparticles as a good plasticizer into PVC molecules.

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