# Synthesis and Microwave Absorption Properties of Doped Expanded Polystyrene with Silver Nanoparticles

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**Abstract**: Polystyrene (PS) is found to become a future major environmental issue and aggressive attempt by scientists to recycle PS into useful functional, recycle materials are becoming recent research trend. Polystyrene has been considered as a potential conductive and wave absorber materials. Doping PS with metal nanomaterials are found to enhance PS physical properties, thus enable the fine tuning of its conductive and wave absorbing properties. In this report, expanded polystyrene as source of PS waste materials are dissolved in tetrahydrofuran (THF), later added into deionized (DI) water to form precipitate polystyrene nanoparticles. This procedure enables easy access of dope silver (Ag) nanoparticles into PS in a colloidal form especially for homogeneity consideration. The UV-Vis spectroscopy (Ultra-Violet Visible), Field Emission Scanning Electron Microscopy (FESEM), Fourier Transformation Infrared Spectroscopy (FTIR), and Vector Network Analysis (VNA) are used to investigate the doped PS nanocomposite of its morphology, molecular vibrations, electrical and electromagnetic properties. The results indicate promising effects of the electrical and electromagnetic properties of doped polystyrene metal nanocomposite as potential conductive and wave absorber material. Results show that these properties are highly dependent on the type of doping materials.

**Keyword**: Expanded polystyrene; Tetrahydrofuran; Silver; VNA; FTIR; Microwave absorption

## 1. Introduction

Microwaves are used extensively in wide range applications including radar technology and radio astronomy, wireless local area networks, smart transport and electronic toll collection systems [1], [2]. Microwave absorber in electronic equipment controls the excessive self-emission of electromagnetic waves and also ensures the undisturbed functioning of the equipment in presence of external electromagnetic wave (EM). Microwave absorbers are also highly demanded in defence and aerospace industries, as the application of microwave-absorbing coating on the exterior surfaces of military aircraft and vehicles helps to avoid detection by the radar [3]. Electromagnetic wave absorbers are materials that effectively attenuate the intensity of electromagnetic waves by absorbing them [4]. Polymers have been studied extensively as promising materials for integrated optical devices due to the broad spectrum of possible applications in data transmission and processing systems [5]. They have become a very attractive for photonic devices because they are easily processed, offer high flexibility, tailor-made properties and have a relatively low cost [6]. In conventional linear polymers such as poly methyl methacrylate (PMMA), polystyrene, polycarbonate have showed the great potential for their use as waveguides at relatively short wavelengths [6] .

Polystyrene (PS) has been chosen as the polymer matrix due to its good thermal

properties, controllable dielectric constant and reasonably light weight [7]. Also PS is widely used in several applications because of its heat durability, nontoxicity, mechanically strength, and thermally non degradable properties. Polymer nanocomposites have attracted great attentions due to the significant roles of nanoparticles (NPs) in enhancing the optical, electrical, magnetic, and mechanical properties [8]. It is well known that the state of particles dispersion is an essentially important in nanocomposites, which is determined by the competition between particle-particle interaction and particle-polymer interaction. Attractive interaction between particles is very common in polymer nanocomposites, which may result in agglomeration of particles and the smaller particle size [7].

Silver nanoparticles (NPs) are used in many applications, such as optics, electronics, gas sensors, catalysis and biomedicine. The properties relevant for these applications depend on the size of the particles [9]. The studies on optical properties of polymers have attracted much attention in view of their application in electronic and optical devices. The optical properties are studied to achieve better reflection, antireflection, interference and polarization properties [4]. There are been recent researches on the microwave dielectric properties and absorption behavior of polymers and composites. In this study, polystyrene and silver nanoparticles were synthesized and their chemical properties were investigated. Also, doped polystyrene with silver nanoparticles derivatives was assessed for application as waveguide absorption.

## 2. Experimental

### 2.1 Synthesis of polystyrene particles

The synthesis of polystyrene particles via nanoprecipitation technique was adopted from Rajeev et al., [10]. Expanded Polystyrene (EPS) waste was obtained from packing material and heated to 150 $^\circ$C in a hot air oven for 12 hours to remove any volatile matters that may agglutinate. The expanded polystyrene was then weighed and diluted in tetrahydrofuran (THF) at the ratio of 2mg/ml. The EPS/THF was mixed with deionized water using magnetic stirrer and

micropipette in a ratio of 1:10, to evaporate the THF the sample was loaded into an oven at 50 $^\circ$C for 12 hours and later centrifugation was used, to remove water and finally achieved the end product needed.

### 2.2 Synthesis of Ag nanoparticles

Chemical reduction technique was used to synthesize silver (Ag) nanoparticles using sodium borohydride $NaBH_4$ as a reduction agent. From this technique, 30 mL of 0.002M sodium borohydride ($NaBH_4$) was prepared in an Erlenmeyer flask. Magnetic stir bar was added into the solution and placed into an ice bath on a magnetic stirrer. 10 mL of 0.001M silver nitrate ($AgNO_3$) was added by dropping into stirring $NaBH_4$ solution at approximately 1 drop per second. By mixing both solutions, Ag ions were reduced and clustered to form monodispersed nanoparticles. 0.3 wt% of polyvinyl pyrrolidone (PVP) was added to the solution to prevent agglomeration between the nanoparticles.

### 2.3 Fabrication of PS/AgNPs

The PS/AgNPs nanocomposite was fabricated through in-situ method, the polystyrene-to-silver nanoparticles ratio varies between 1:4 and 1:8. The samples were then transferred to eppendorf tube for homogeneity and mixed by using a Vortex mixer for one minute at high rpm, later ultrasonic agitation for 45mins at high frequency before coated. Samples were cut precisely to fit the waveguide sample holders in order to minimize the reflection loss via gap between the film and waveguide sample holders. A pure PS film was used as a reference material.

### 2.4 Characterization techniques

The colloidal Ag nanoparticle was analyzed by UV-Vis measurements with a 1 cm path length quartz cuvette using a UV-1800 Spectrophotometer (Shimadzu) at room temperature in the range 300-900 nm. Morphologies of the samples were observed using Field Emission Scanning Electron Microscopy (FESEM, JEOL JSM-7600F) and coated with platinum before characterization.

FTIR analysis was performed using a Perkin Elmer FTIR Spectrometer LR 64912C, N3896 equipped with a universal Attenuated Total Reflectance (ATR) sample stage and a spectrum express FTIR software V1.3.2 Perkin Elmer LX100877-1. The sample molecular structure is determined within the range of 4000–400 cm$^{-1}$ with a resolution of 4 cm$^{-1}$. The microwave absorption was carried out using a Vector Network Analyzer (VNA) to determine the values of complex relative permittivity in the 2.0 MHz-13 GHz range by using coaxial reflection technique. During measurement, samples were coated on silicon wafer and mounted in a coaxial sample holder to waveguide adapters which are connected to the ports of VNA. Two ports calibrations were carried out on the adapter surfaces using the standard X band waveguide calibration kit before placing the samples for the measurements.

### 2.4.1 Microwave absorption theory

The microwave absorbers are mainly characterized using electromagnetic properties in terms of the complex permittivity and the complex permeability. The complex permittivity arises from the dielectric polarization of the materials and defines as [11]–[15].

$$\varepsilon = \varepsilon' - j\varepsilon'' \qquad (1)$$

Where $\varepsilon'$ is the real part of complex permittivity (known as the dielectric constant) and $\varepsilon''$ is the imaginary part of complex permittivity [3].The real and imaginary parts of complex permittivity are mainly associated with the stored energy and energy dissipation of the material. Energy loss in a material is depends on the illuminated by electromagnetic waves comes about through damping forces acting on polarized atoms and molecules and through the finite conductivity of a material [16]–[18]. The dielectric loss tangent of the material is defined as

$$\tan \delta = \frac{\varepsilon''}{\varepsilon'} \qquad (2)$$

## 3. Results and discussion

### 3.1 UV-Visible analysis of silver nanoparticles

Fig. 1 shows the absorption spectrum of the silver nanoparticles. Sample presents the characteristic surface Plasmon of silver nanoparticles present a narrow band with a maximum at 420 nm. It was reported that the absorption spectrum of spherical silver nanoparticles present a maximum between 420 and 450 nm with a blue or red shift when particle size diminishes or increases [19]–[22]. The results further indicated that the formation of silver nanoparticles via chemical reduction method was very successful.
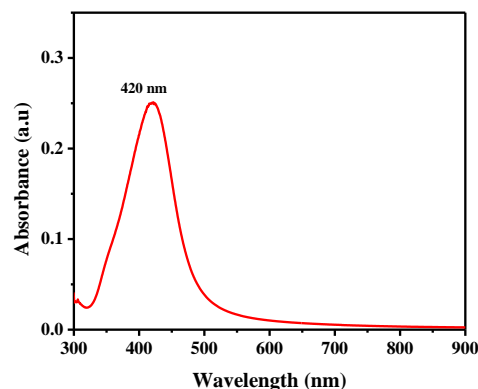


**Fig. 1** UV–Vis spectrum of the silver nanoparticles synthesized

### 3.2 FESEM analysis

The morphology of the PS and PS:Ag nanocomposites were studied using the FESEM and results are showed in Fig. 2(a-c), reports have shown that the incorporation of metals nanoparticles into polymer can improve the properties or create a new functionalities [23]. The important factors involved in improving the properties of polymer are the type, size, shape and ratio of the metal nanoparticle dispersion in polymer and interfacial interaction between organic and inorganic nanoparticles, fig. 2a show un-uniform size of polystyrene particles. FESEM image of PS/AgNPs (Fig. 2b&c) clearly reveals that AgNPs are dispersed at the surface and embedded within the polystyrene; the structures

show clear boundary within the matrix that silver nanoparticles indicates a weak interfacial interaction between aggregates and PS, which is consistent with the results obtained by FTIR spectrometry. These results are clearly show that the AgNPs were successfully embedded into polystyrene and modified the functional properties of the polystyrene.
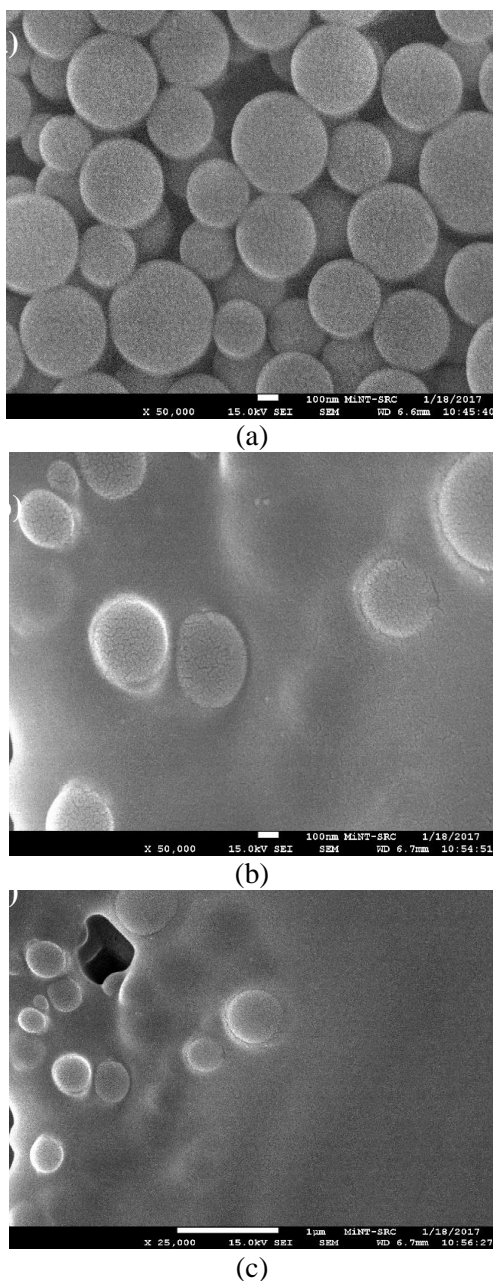


(a)



(b)



(c)

**Fig. 2** FESEM images obtained for (a) PS (b) PS:AgNPs (1:4) PS:AgNPs (1:8) nanocomposite.

### 3.3    FTIR analysis

To confirm the chemical structure of the PS and PS:Ag nanocomposites, FTIR spectra analysis of PS and PS:Ag were performed. Fig 3a-c presents FTIR spectra of the PS, PS:Ag 1:4 and PS:Ag 1:8 nanocomposites. From fig 3a, the spectrum shows the presence of the characteristic bands of PS at 3060 $cm^{-1}$, 3026 $cm^{-1}$, which corresponds to the =C-H stretching due to the aromatic ring, bands at 2907 $cm^{-1}$ 2843 $cm^{-1}$, is attributed to the symmetrical and asymmetrical stretching vibration of $CH_2$, bands at 1600 $cm^{-1}$, 1494 $cm^{-1}$, 1445 $cm^{-1}$ are correspond to stretching vibration of the C=C bond on the benzene ring, bands at 1112 $cm^{-1}$, 1055 $cm^{-1}$ and 882 $cm^{-1}$, which corresponds to the =C-H stretching due to the aromatic ring, and C-H out of plane bending vibration respectively. [24]-[25]. In addition, the band at 3068 $cm^{-1}$ is for stretching vibration of O-H, which indicates the existence of hydroxyl. The hydroxyl may appear from water. After doping, Fig. 3(b-c) presents FTIR spectra of the PS:Ag nanocomposites. For the PS/Ag (1:4) nanocomposites, spectrum shows characteristic bands at 1773 $cm^{-1}$, 1636 $cm^{-1}$, 1292 $cm^{-1}$ 1084 $cm^{-1}$ and 877 $cm^{-1}$ which correspond to the aromatic ring and aliphatic C–H and –CH stretching, respectively. For the PS:Ag (1:8), the spectrum shows characteristic bands at 1773 $cm^{-1}$, 1636 $cm^{-1}$ and 1301 $cm^{-1}$ are assigned to the aliphatic C–H and –$CH_2$ respectively; where some bands were found collapse, reduced in intensity and shifted compared with the PS.
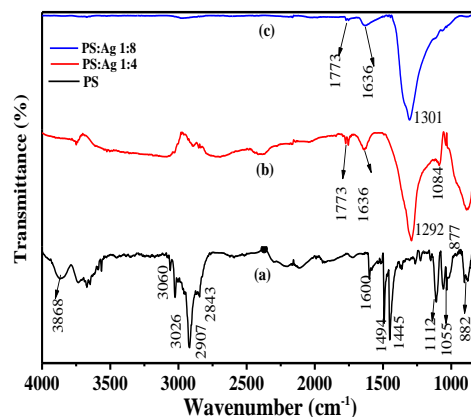


**Fig. 3** FTIR spectra of (a) PS (b) 1:4 (c) 1:8 PS:AgNPs nanocomposites.

### 3.4 Microwave absorption

#### 3.4.1 Permittivity spectra analysis

The permittivity of the PS and PS;AgNPs were measured using waveguide method. Usually, the complex permittivity of composite is an equivalent permittivity since it can not only be controlled by conductive filler but also be significantly influenced by polymer matrix. The complex permittivity of composite is decided by volume fraction of conductive filler [11]. However, the volume fraction of conductive filler is influenced by the density of polymer matrix, when weight fraction is used to compare the EM absorption properties. Fig. 4a&b shows the real and imaginary part of the complex relative permittivity spectra for PS and PS/AgNPs (1:4 & 1:8), where the parameter real part $\varepsilon'$ represents the charge storage (dielectric constant) whereas the parameter of imaginary part $\varepsilon''$ is to measure dielectric losses. Dispersion of AgNPs nanoparticles filler in PS matrix leads to interfacial polarization and relaxation effects [26]. All these factors are responsible for high values of real and imaginary part. Fig. 5a for 1:4 and 1:8 shows that as the ratio of AgNPs increases, the dielectric constant increases from 9.03 to 24.28 whereas the imaginary part also increases (fig. 5b) from 0.8 to 8.9.

The real part of the complex permittivity is almost constant in the whole X-band of microwave frequency for a given silver nanoparticles concentration, it increases with the significant increase of silver nanoparticles in the polystyrene matrix. The imaginary part of the complex permittivity (loss factor) increases with the addition of silver nanoparticles which could be attributed to the conversion of low loss PS into the lossy dielectric due to presence of high ratio of silver nanoparticles conducting fillers. It can be concluded that the PS/Ag nanocomposite with higher filler content appears to be a promising candidate for microwave absorber applications. The increased in conductivity of PS depends on the presence of Ag nanoparticles which could account for the enhanced reflection of EM wave from both external as well as internal surface.
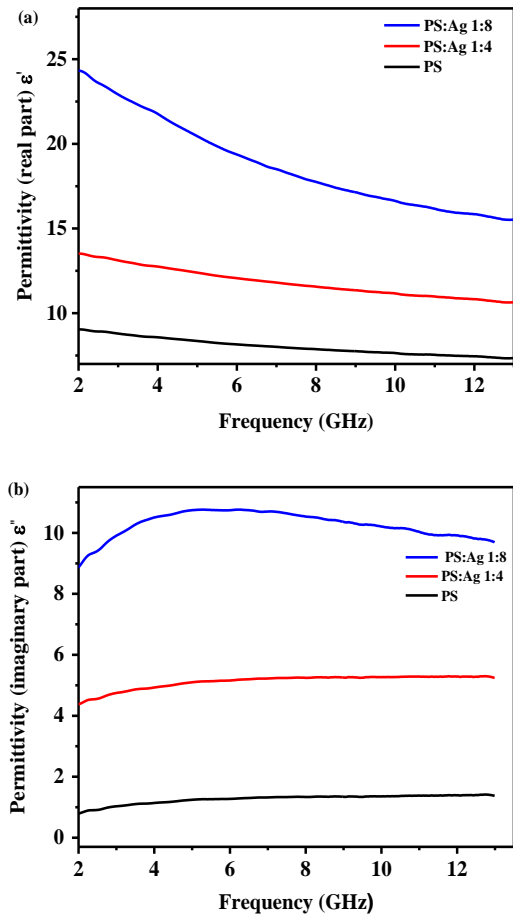


**Fig. 4** Frequency dependence of (a) real part (b) imaginary part of relative complex permittivity for PS and PS:AgNPs nanocomposites.

#### 3.4.2 Conductivity and dielectric loss

Polymer matrix has a significant effect on the amount of filler required for electrical percolation [12]-[13],[26]. The electrical conductivity of polymer matrix also influences the permittivity of composite. Fig. 5a&b shows the conductivity and dielectric loss tangent of PS and PS/AgNPs nanocomposite at different ratios. Fig. 5a reveals that for neat PS the conductivity value ranges from (0.08-0.99), for PS/AgNPs 1:4 (1.50-2.97) and for PS/AGNPs 1:8 (3.70-6.90) which indicate that as filler increases the value of conductivity increases. The increase in permittivity can be attributed to the increase in electrical conductivity. Fig. 5b shows dielectric tangent loss factor (tanδ) of PS (0.08-0.19), PS:AgNPs 1:4 (0.34-0.47), and PS:AgNPs 1:8 (0.72-097), in

the range of frequency 2-13 GHz. It was observed that in all cases the tanδ value of nanocomposites is higher than neat PS. The higher dielectric loss value for PS:AgNPs is probably due to absorbance of EM waves due to internal reflection. In addition it was also observed that with increasing AgNPs loading, the PS/Ag nanocomposites show increasing dielectric loss. High conductivity of Ag nanoparticles is probably responsible for this observation. Ag has the highest electrical conductivity among other metals so it contains considerable amount of free electrons for movement. As the collision of particles occurs among each other and causes hindrance in movement, during collision energy of EM wave transferred in to heat to be dissipated. This could be responsible for the increments in dielectric loss of the materials [27-29].
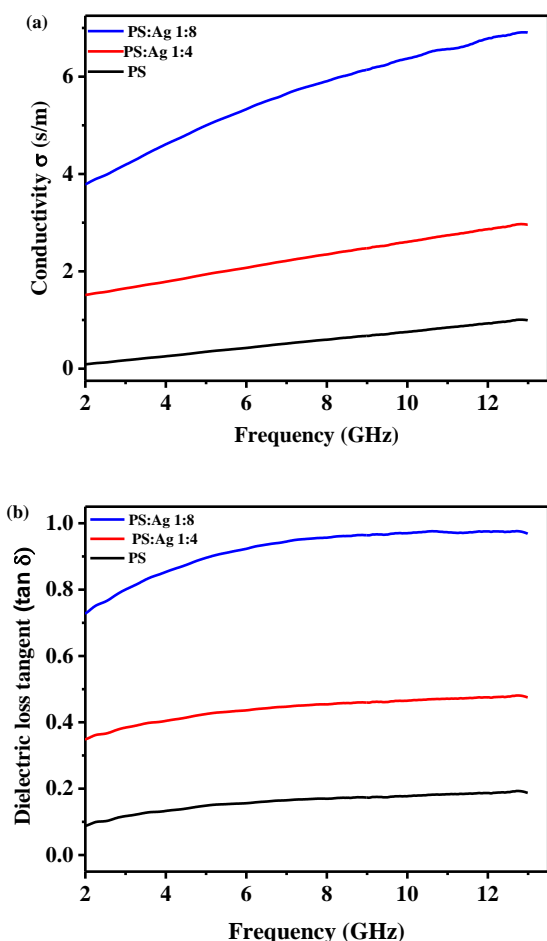


**Fig. 5** Frequency dependence of (a) conductivity (b) dielectric loss tangent for PS and PS:AgNPs nanocomposites with different ratio.

## 4. Conclusion

In conclusion, silver nanoparticle was established by chemical reduction method. UV-VIS absorption results confirmed formation of silver nanoparticles synthesized by chemical reduction method. PS:AgNPs nanocomposites was successfully prepared by ultrasonic technique. This method provides an alternative approach for the preparation of metal doped polystyrene. FESEM and FTIR results confirm the formation of PS/Ag composites, which had both properties of the polystyrene and surface properties of silver nanoparticles. NVA results revealed that both permittivity and electrical conductivity have showed increases as the filler increases compared with neat PS. PS:Ag nanocomposite with higher filler content appears to be a promising candidate for microwave absorber applications. It is also believed that the prepared PS:Ag composites have other potential applications such as catalysis, antibacterial and optical.

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